REPORT OF PETROLEUM AND NATURAL-GAS BRANCH FISCAL YEAR 1948

BY R. A. CATTELL AND OTHERS

* * * * * * * * * * **Information Circular 7532**

A Century of Conservation

1849 1949

UNITED STATES DEPARTMENT OF THE INTERIOR
Oscar L. Chapman, Secretary
BUREAU OF MINES
James Boyd, Director

Work on manuscript completed March 1949. The Bureau of Mines will welcome reprinting of this paper, provided the following footnote acknowledgment is made: "Reprinted from Bureau of Mines Information Circular 7532."

December 1949

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REPORT OF PETROLEUM AND NATURAL-GAS BRANCH, FISCAL YEAR 1948[1/]

by

R. A. Catlell[2/] and others

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1/ To conform with standardized nomenclature in the Government organization structure, the unit name was changed from division to branch on January 1, 1948.

2/ Chief, Petroleum and Natural-Gas Branch, Bureau of Mines, Washington, D. C.

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SUMMARY

The Bureau of Mines actively conducted a well-coordinated research program during the past fiscal year on problems dealing with the production of oil and gas, transportation of natural gas, chemistry and refining of petroleum, thermodynamic properties of hydrocarbons, and the processing and utilization of incombustible helium gas. These particular reserach phases, comprising the presently scheduled activities, are integral parts of a broad program selected soon after the war as suitable for Bureau of Mines study, to meet immediate needs for specific information on petroleum and natural-gas problems of national scope. Important progress was made and many technical reports were finished during the year.

Several reports were published on gas-condensate production problems, one giving the results of laboratory tests of relative merits of various steels and alloys for resisting the corrosion that occurs in high-pressure gas-condensate wells. Research was continued, using the Bureau's windowed cell, to determine the characteristics of gas-condensate fluids, and an important paper on the phase relations of these fluids at low temperatures was published.

An important part of the Bureau of Mines petroleum production research program for many years has been the engineering study of type oil fields. This year reports were completed on the Lake Creek, Sheridan, and West Red River fields, Tex.; the Atlanta field, Ark.; and the Boggs field, W.V. Other fields under study and for which reports will be issued are the Carthage and New Hope fields, Tex., and the Weber pool, Okla.

Special studies to determine the characteristics of the oil-gas solutions as they exist within the native reservoir rocks have been in progress in the North Lindsay field, Okla.; the Elk Basin field, Wyo. and Mont.; and the Rangely field, Colo. The North Lindsay study brought to light several unusual physical properties of the oil as it is found in this deep-seated reservoir. For instance, its viscosity is less than that of water, and more than 2 barrels of the initial reservoir oil must be produced to yield 1 barrel of "stock-tank oil." In the Elk Basin and Rangely fields the oil-gas solution varies in composition within the reservoir, depending upon structural location.

Engineering studies were continued on well spacing and on drilling fluids with special emphasis on obtaining uncontaminated cores, or cores for which the flushing action of the drilling fluid can be determined accurately. In connection with research on production of oil by secondary recovery methods, progress was made in studies of conditioning water for subsurface injection, of input rates and pressures for water-flooding oil sands, and of the selective plugging the more permeable mediums to prevent or retard channeling of the injected fluid.

The availability of fuels for all types of internal-combustion engines still is the primary research project in petroleum chemistry and refining. This research program is subdivided into a series of problems under four main topics: (1) Raw-material studies; (2) relationships of fuel consumption, properties, and performance; (3) utilization of petroleum products; and (4) analytical methods, which include chemical and physical property determinations.

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During the year the findings of a Bureau of Mines study of the sulfur contents of crude oil were published in two trade journals. This part of the raw-materials research showed that the total production of high-sulfur crude oils reached a new high in 1946. Also a new report presenting analyses of crude oils from 283 important fields in the United States was issued. A bibliography was published to present a finding list of over 2,400 crude-oil analyses that the Bureau of Mines has completed and reported since the inception of its crude-oil survey.

In connection with the second part of this research program dealing with the relationship of fuel composition, properties and performance, reports were prepared on both gasoline and Diesel fuels. Composition and performance characteristics of the naphtha portions of Oklahoma City, Okla., and Santa Barbara, Venezuela, crude oils were studied with the aid of superfractionation and the results reported. Moreover, a preliminary report of studies on the composition and physical properties of Diesel fuels was presented before the Society of Automotive Engineers in Detroit in January 1948.

In connection with the utilization phase of the program, the National Motor Gasoline Survey was continued, and the results of the tests for the Summer of 1947 and the Winter of 1947-48 were published. The Aviation Gasoline Survey initiated last year was continued, and the first report (for March 1947) was issued. The second report is in press at the end of this fiscal year, and this series of aviation gasoline reports will be rapidly brought up to date.

Several studies aimed at improving analytical methods and determining the properties of narrow-boiling fractions from crude oils were in progress during the year. Research on sulfur compounds and their occurrence in petroleum was pursued actively. Three sulfur compounds were prepared and purified, and portions were sent to the National Bureau of Standards for distribution to interested laboratories. Physical and thermodynamic properties of these compounds are being determined in the laboratories of the Bureau of Mines.

Additional thermodynamic data were obtained by low-temperature, vapor-phase, and combustion calorimetry. Vapor-pressure measurements and calculation of thermodynamic functions by statistical methods were initiated. Several reports were presented in scientific journals to make the results of this work accessible to the public.

The natural-gas research program includes studies of the productivity of high-pressure gas wells, factors influencing flow of gas in pipe lines, ways and means of removing nitrogen from natural gas, and the development of a water-content recorder for use on natural-gas transportation systems.

An important part of the Bureau's program deals with research on helium. This includes a survey to determine the Nation's helium resources, and this was continued actively. One important result of development research was installation of equipment that makes it possible to raise the purity of the helium produced by the Bureau of Mines large-scale extraction plants to 99.8 percent or better. Research on utilization included studies on uses of helium in metallurgy, welding, and as a tracer gas to mark the course followed by oil and gas in flowing through the productive formations in the native underground reservoirs.

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INTRODUCTION

In the more than 2 years that have elapsed since the ending of hostilities, the Petroleum and Natural-Gas Branch of the Bureau of Mines has reoriented its activities to its main normal functions. This is evidenced by the close attention being paid to technical detail and by the careful way in which scientific relationships throughout the various research problems are being worked out - impossible under war conditions.

To maintain a good balance between industrial needs and Government research possibilities, members of the Branch have given continued careful scrutiny to the types of problems best adapted to study by the Bureau in the national peacetime economy. In these evaluations, account has been taken of changes in emphasis that have been necessary in the program set up immediately after World War II. In so doing, it has been timely to pose the question: Is the branch using its energy, manpower, and funds to the best advantage in accomplishing two of its main normal functions? Stated briefly those functions are:

(1) To increase the total quantity of petroleum and natural gas that can be withdrawn from beneath the earth's surface.

(2) To obtain better utilization in manufacturing products from these natural resources.

No two persons will reach the same conclusions regarding the scope of a Federal research agency. However, few persons will disagree on the premise that Government and industry should work hand in hand toward attaining these named objectives.

The list of publications of a research organization is one of the surest measures of its accomplishment. The number and scope of technical subjects investigated and reported upon during the last fiscal year only are reflected in the footnotes of the body of this report. To make all of its reference material more readily available to those who wish to study the technology of the petroleum industry, the branch again revised and brought to date its selected list of Bureau of Mines publications dealing with petroleum, natural gas, helium, oil shale, and related subjects. Through the years this reference has grown from a mere numerical listing comprising a few pages of titles of technical publications until now the January 1, 1948, edition contains 166 pages. The listing of title references has been divided under the following 12 main headings:

Drilling oil and gas wells
Petroleum production
Geophysical prospecting
Chemistry and refining of petroleum
Storage and transportation of petroleum and petroleum products
Safety and health in petroleum and natural gas industries
Natural gas and natural-gas products
Natural gasoline
Helium and related subjects
Oil shale and shale oil
Thermodynamic properties of petroleum hydrocarbons
General and miscellaneous publications

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In addition, these "finding" lists are augmented by author, subject, and publication number indexes; the libraries and other organizations throughout the country where all Bureau of Mines publications are on file are given; and a list of Bureau of Mines motion-picture films - another feature of its visual-educational work in the mineral industries - is included.

The library at the Bartlesville, Okla., Station has increased its accession list to approximately 6,000 bound volumes dealing with petroleum and the subjects relating thereto; and the number of volumes of reference material in the more recently opened library of the Laramie, Wyo., station likewise is being increased consistently. These two libraries, with technical librarians in charge, and the well-stocked reference shelves at Franklin, Pa., Dallas, Tex., Amarillo, Tex., and San Francisco, Calif., are available for public use in addition to serving the personnel of the respective field headquarters. There is a growing awareness that reliable technical references within easy reach are just as important "tools" in the conduct of research as precision measuring instruments. The value of these reference sources in various parts of the country that have been named can not be placed too high. They not only serve their own immediate reading patrons but also cooperate informally with other public and privately owned technical libraries. Many calls for reference material are received from them and from individuals.

To avoid any confusion in the minds of those who have been accustomed to refer to this Governmental unit as a "division," a brief explanation is given here:

Throughout a period of more than 25 years, this research group in the field of petroleum technology has been called the Petroleum and Natural-Gas Division. It was originally established in the Bureau of Mines as the "Petroleum Division" on July 1, 1914, but a few years later the name was expanded to include the companion hydrocarbons, natural gas. More intimately, its members usually have called their organization "The division." However, on December 18, 1947, in conformance with a congressional recommendation to standardize nomenclature in the Government organization structure, the Director specified[3/] that "the present branches of the Bureau of Mines shall be known as Divisions, and the divisions as Branches." Accordingly, all future reference to this group concerned with petroleum technology will be in terms of the Petroleum and Natural-Gas Branch.

The Petroleum and Natural-Gas Branch has only a small headquarters staff in Washington, D. C. Its largest centers for petroleum research are the Petroleum Experiment Station at Bartlesville, Okla., and the Petroleum and Oil Shale Experiment Station at Laramie, Wyo. Petroleum field offices are at San Francisco, Calif.; Dallas, Tex.; and Franklin, Pa. A suboffice is maintained at Wichita Falls, Tex. Field studies are conducted from the field offices and suboffice, as well as from the experiment stations. Two of the field offices have small laboratories for supplementing the field studies, and the experiment stations have more complete facilities for conducting laboratory and field investigations. This branch also conducts a helium research program and operates large-scale production facilities to furnish helium to Federal and non-Federal users. In this connection, it operates and maintains

3/ Bureau of Mines Administrative Order 537.

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helium-bearing gas fields in Potter County, Tex., and San Juan County, N.M.; helium plants at Amarillo and Exell, Tex., Otis, Kans., and Shiprock, N.M.; and a helium-research laboratory at the Amarillo plant.

ACKNOWLEDGMENTS

This information circular is based upon reports submitted by the supervising engineers of the six field headquarters of the branch. These are:

H. C. Fowler, Petroleum Experiment Station, Bartlesville, Okla.
H. P. Rue, Petroleum and Oil Shale Experiment Station, Laramie, Wyo.
C. W. Seibel, Bureau of Mines Helium Plants, Amarillo, Tex.
H. C. Miller, Petroleum Field Office, San Francisco, Calif.
C. B. Carpenter, Petroleum Field Office, Dallas, Tex.
S. S. Taylor, Petroleum Field Office, Franklin, Pa.

Almost all scientists and engineers of the branch contributed directly or indirectly to the preparation of this report. Special mention is due C. J. Wilhelm, R. V. Smith, C. H. Riggs, H. M. Smith, C. C. Ward, Gustav Wade, H. T. Rall, C. M. McKinney, H. M. Huffman, N. A. C. Smith, E. M. Frost, Jr., R. H. Espach, J. S. Ball, E. M. Tignor, B. F. Grant, G. B. Shea, F. G. Miller, and G. L. Gates for their assistance in assembling and preparing the material for many sections of this report.

In conducting research on petroleum, natural gas, and helium, the Bureau of Mines enjoyed the hearty cooperation of the oil and gas industry, and acknowledgment is made for this assistance. Also, the work was aided greatly through cooperative agreements with the State of Oklahoma, the Kansas State Board of Health, the Arkansas Oil and Gas Commission, the University of Wyoming, the Texas Technological College, the American Petroleum Institute, the Coordinating Research Council, the Natural-Gas Department of the American Gas Association, the Natural Gasoline Association of America, the Pennsylvania-Grade Crude-Oil Association, and the North Texas Oil and Gas Association.

OIL AND GAS DEVELOPMENT AND PRODUCTION

Production research of the Bureau of Mines has been continued along the lines of the coordinated program outlined by the Petroleum and Natural-Gas Branch after the end of the last war. The important technical problems of the petroleum and natural-gas industry were evaluated, and a program was developed on the basis of immediate need for specific information by industry, suitability of the research projects as Bureau of Mines undertakings, and personnel and equipment available for conducting the work. Emphasis is placed on the recovery of more oil during the early stages of production, to be accomplished by developing new and improved production practices, resulting in more efficient use of reservoir energy.

Progress in this research is shown by the publication of three reports during the past year, the completion of two manuscripts on engineering field studies, and six additional reports in various stages of completion. One of the published reports presented data on the specific volumes and liquid : gas ratios of a natural gas and four mixtures of condensate with the gas at temperatures in the range of minus 65° to plus 100° F. Another published

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report included the experimental results obtained in measuring the compressibilities of a low-nitrogen-content natural gas and of two mixtures of the natural gas with added nitrogen. The third report presented the results of laboratory tests of relative merits of various steels and alloys for resisting the corrosion that occurs in high-pressure gas-condensate wells.

Low-temperature data, such as those obtained with the windowed cell - a specially designed laboratory apparatus that makes possible the determination of the physical characteristics of gas-condensate fluids at relatively low temperatures - will aid in the correlation of data on phase relations at high temperatures and pressures significant in production and refining practice. Moreover, the data have direct application in the processing of gas-condensate fluids and in the transmission of natural gas at low temperatures. The information on the liquid : gas ratios of the fluids in the region of the critical state can be a useful guide in the design of equipment for liquefying and storing natural gas at low temperatures.

Characteristics of Gas-Condensate Fluids

Fundamentals of physical chemistry and thermodynamics are utilized in the investigation of the properties of natural hydrocarbon mixtures in the range of pressures and temperatures that are significant in the production and refining of petroleum. The results of research before 1934 indicated the need for knowledge of the phase relations and flow characteristics of gas-condensate fluids, and since then the problem has been under continuous study. Through the years apparatus and procedures have been developed for determining the properties of gas-condensate fluids, although the work necessarily was conducted in steps and now is resulting in the accumulation of basic data valuable in the application of engineering principles to gas-condensate reservoirs. Using a windowed cell developed by Bureau of Mines engineers at the Bartlesville Station, information was obtained regarding the properties of hydrocarbon mixtures at low temperatures[4/] to supplement and to aid in correlating extensive data that have been obtained at flowing wells in the field by means of mobile equipment.

An unexpected finding was that the critical temperature of the separator gas was higher than the critical temperature of the gas-condensate fluid flowing from the well. It is significant that the experimentally determined critical temperatures of the mixtures did not vary with the composition on an additive basis. For these mixtures the critical temperature, which is a particularly pertinent physical characteristic in production practice, was found to be higher the more gas and the less condensate they contained. The measured and the estimated values of the critical temperature may differ by 7 percent, and critical pressures determined by the two methods may differ as much as 100 percent.

Figure 1 illustrates the type of data developed by the windowed cell and shows graphically the liquid : gas ratios of a mixture of natural gas and gas

4/ Eilerts, C. K., Barr, V. L., Mullens, N. B., and Hanna, Betty, Phase Relations of a Gas-Condensate Fluid at Low Temperatures, Including the Critical State: Petrol. Eng., vol. 19, No. 5, February 1948, pp. 154-180.

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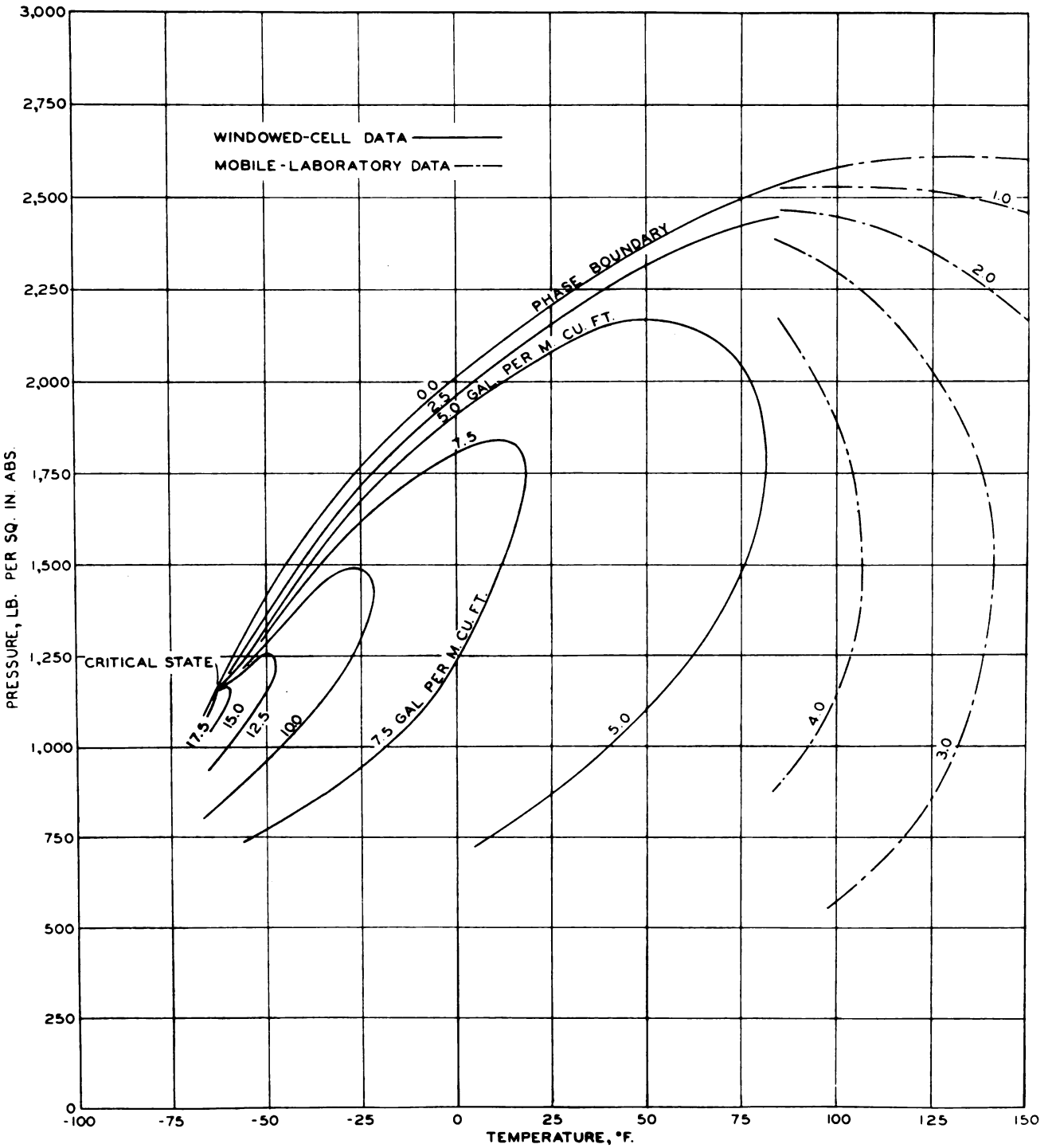

Figure 1. - Liquid:gas ratios of a produced gas - condensate fluid at low temperatures.

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condensate in the proportions actually produced from a gas-condensate well. The continuous lines, which converge at a point identified as the "critical state," show for given pressures and temperatures the gallons of liquid hydrocarbons present in a fluid with 1,000 cubic feet of natural gas. The "phase boundary" shows the limits of pressure and temperature at which the fluid is in two phases; at all points outside the phase-boundary curve the fluid is in a single-phase state, either gaseous or liquid, and at all points within the fluid contains both liquid and gas; the proportions of the phases depend upon the pressure and temperature. The data obtained with the mobile laboratory in the field, shown by dashed curves at temperatures above 85° F., substantiate the data, obtained with the windowed cell below 85° F., on a sample transported to the laboratory.

Before development of the mobile laboratory and the windowed cell for investigating the characteristics of gas-condensate fluids, an equilibrium cell had been constructed to study the specific volumes and phase-boundary properties of the fluids. The work with the equilibrium cell led to a study of the effect of added nitrogen on the compressibility of natural gas.5/ Most of the methods devised for computing the compressibility factor of a natural gas from its components are based on correlations of the properties of the hydrocarbon components. As the molecular structure and physical characteristics of the paraffin hydrocarbon components that predominate in natural gas are related, such methods are reliable for low-nitrogen-content gases. However, nitrogen, a common component of natural gas, is chemically unlike hydrocarbons and has different compressibility characteristics. As a result, reliable methods of computing compressibility factors must give consideration to the effect of nitrogen when it is present in natural gas in relatively high concentration.

Compressibility data were obtained on a low-nitrogen-content natural gas and two mixtures of the natural gas and added nitrogen within the temperature range 32° to 280° F. at pressures up to 5,000 psi (pounds per square inch). It was found that the volumes of mixtures of natural gas and nitrogen in different proportions were as much as 3 percent greater than the volumes of the separate constituent gases at given pressures and temperatures.

Data available in the literature on the compressibility of nitrogen were summarized in a convenient table and chart, and a method was shown for using these data to estimate the compressibility of gases containing nitrogen. The method involves computing the volume of the hydrocarbons and that of the nitrogen separately and correcting the sum of the volumes by means of the additive volume correction factor. The compressibility factors of natural gases containing up to 20 percent nitrogen may be computed with an accuracy that is comparable with the accuracy possible in estimating the compressibility of the hydrocarbon components alone.

Gas-Condensate-Well Corrosion

Control of corrosion in gas-condensate wells is an engineering problem involving high costs. The nature and extent of the corrosion vary from field

5/ Eilerts, C. K., Carlson, H. A., and Mullens, N. B., Effect of Added Nitrogen on Compressibility of Natural Gas, part 1: World Oil, June 1948, pp. 129-140; part 2, World Oil, July 1948, pp. 144-160.

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to field, and numerous methods for combating it are practiced. Replacement of tubing, wellhead fittings, and flow lines, continuous or intermittent injection of treating chemicals, periodic inspection of equipment and checking of the efficiency of the control methods, and reduction of rates of flow from wells are all used under varying conditions and reflect the high cost of corrosion. Estimates have been made for a number of important fields that corrosion adds $4 to $5 to the cost of producing a million cubic feet of gas.

Results of extensive laboratory tests of the relative merits of various steels and alloys for resisting the corrosion that occurs in high-pressure gas-condensate wells were published in the trade journal Corrosion.6/ Because of the great expense involved in testing alloys under actual service conditions, laboratory tests were devised to subject commercially available metals and special steel alloys to the corrosive action of gas-condensate fluids with the objective of determining those that have the properties required for service in high-pressure gas-condensate wells subject to corrosion. Bureau of Mines engineers have studied the problem during the last 4 years and have actively cooperated with research committees of the Natural Gasoline Association of America and the National Association of Corrosion Engineers.

The relative resistance to corrosion of 72 alloys and alloy steels was determined in aqueous solutions of carbonic acid, propionic acid, and phenol maintained at 130° F., and the results of the tests were condensed in the chart, (fig. 2). A steel containing approximately 9 percent chromium would provide the best combination of corrosion resistance, physical strength, and cost economy of any of the steels tested. A steel containing 7 percent chromium, although not as effective as the 9-percent chromium steel, would sustain less weight loss than the carbon steel now manufactured to meet A.P.I. Grade J-55 specifications for tubing and would not be subjected to serious pitting corrosion. The laboratory tests indicated that a steel containing 9 percent nickel would not be subject to the severe pitting corrosion that is characteristic of the carbon-steel tubing now used in wells and would be subject to lower rates of weight loss. Tests in the field exposing coupons of metals in the flow stream of wells have indicated that 9-percent nickel steel has relatively high resistance to corrosion by gas-condensate fluids.

Pressure cells and constant-temperature water baths were used to determine the rates of corrosion of the steels and alloys in the liquid corrosive mediums. Figure 3 shows the equipment used and procedure followed in removing from a cell the pint jars containing the metal coupons suspended in the corrosive solution. The cells were mounted in the water baths in such manner that the jars are beneath the surface of the water and are rotated at 9 r.p.m. to provide agitation of the corrosive mediums. The water baths were maintained at 130° F.

Distribution of the weight loss was an important consideration in judging the relative corrosion resistance of the metals. An assembly of photomicrographs of the surface of coupons exposed to the corrosive action of carbonic

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6/ Eilerts, C. K., Greene, Faye, Archer, F. G., Hanna, Betty, and Burman, L. M., Alloying Steels for Corrosion Resistance to Gas-Condensate Fluids, part 1: Corrosion, June 1948, pp. 245-263; part 2, Corrosion, July 1948, pp. 321-356.

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Figure 2. - Relative resistance of alloys and alloy steels to corrosion by carbonic and propionic acids and phenol.

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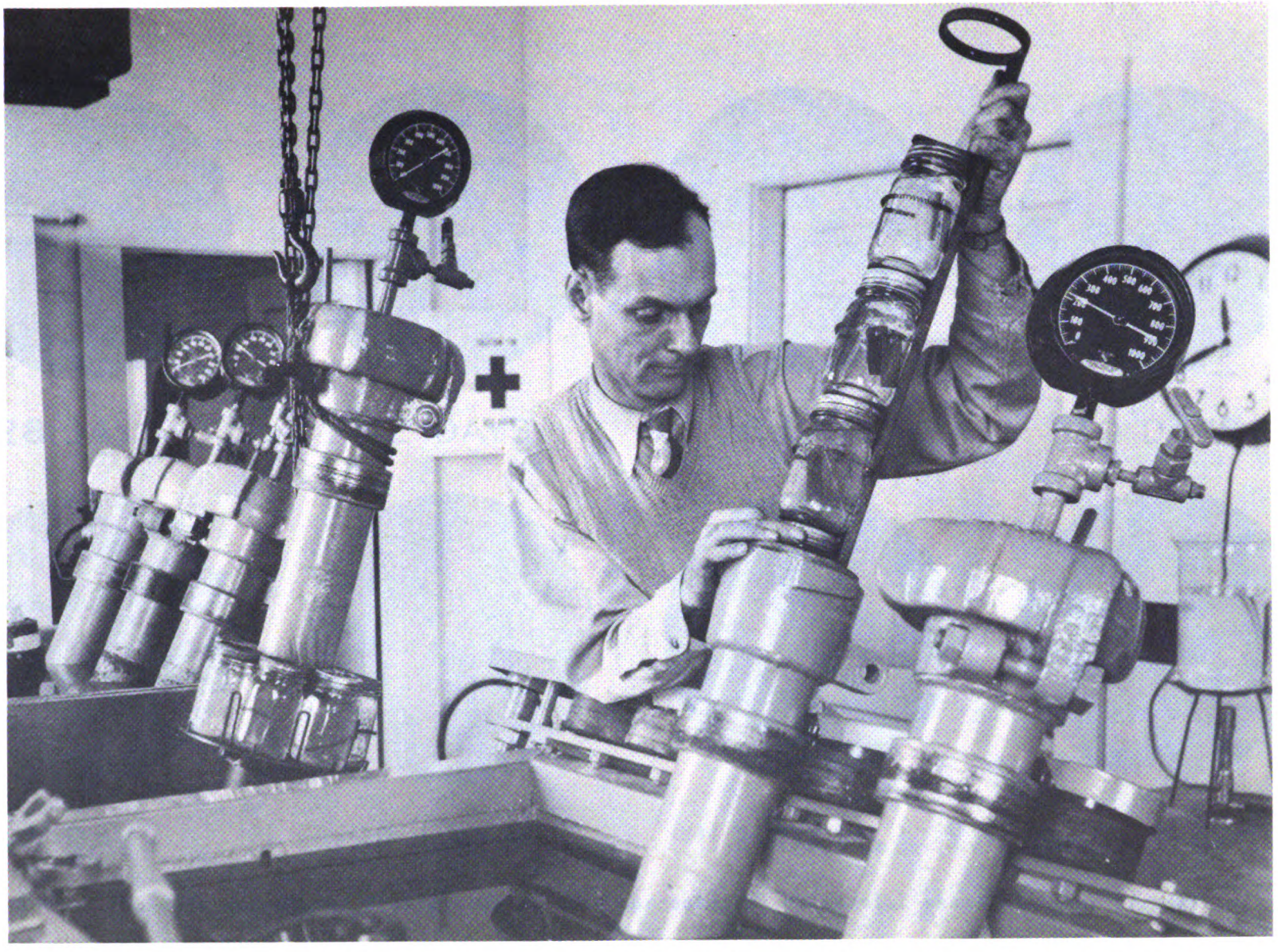

Figure 3. - Equipment used in subjecting steel and alloy metals to the corrosive components of gas-condensate fluids.

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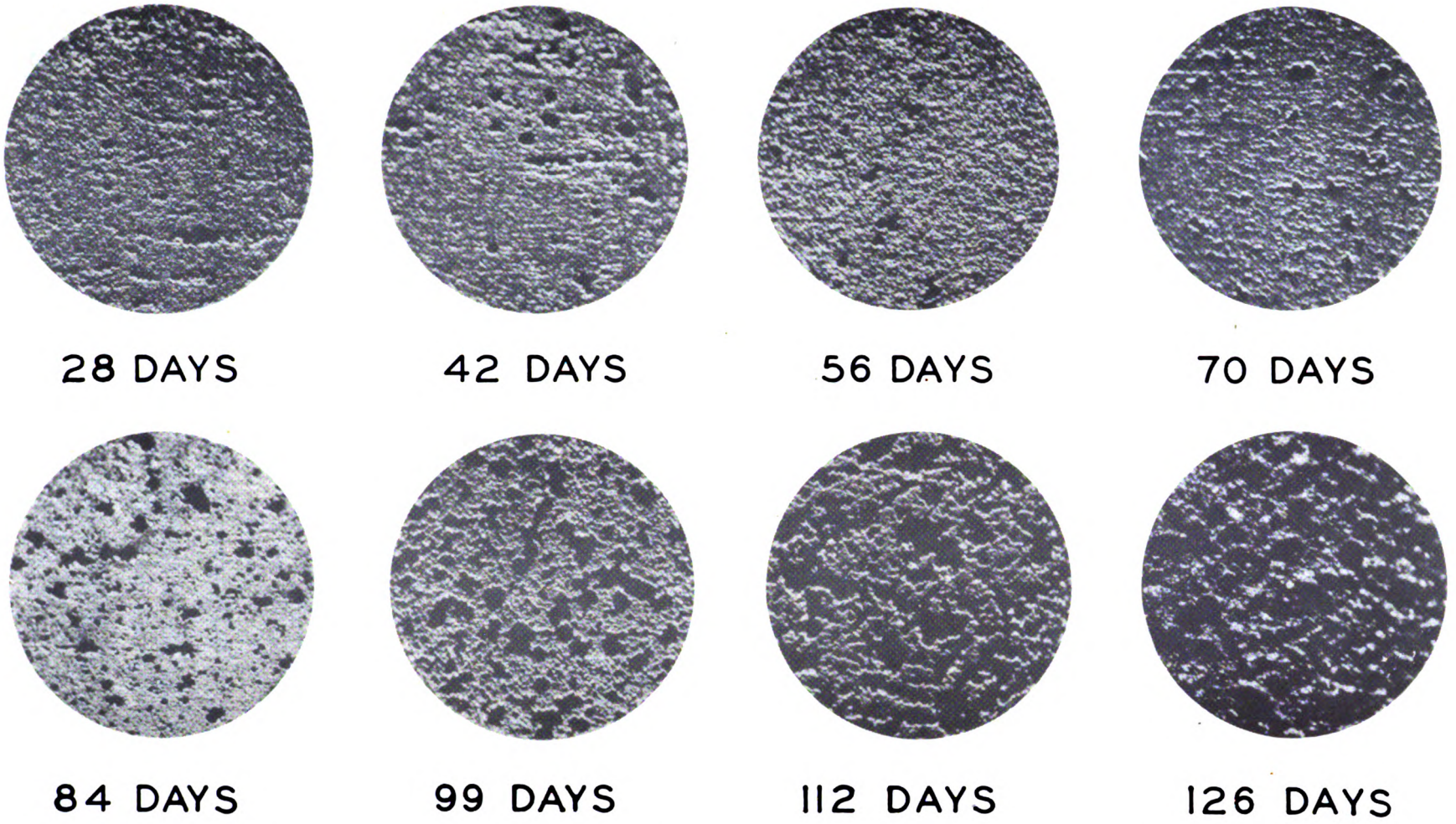

Figure 4. - Photomicrographs of progressive pitting corrosion of commercial sheet steel by carbonic acid.

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acid is shown in figure 4. The coupon exposed for 28 days shows the beginning of a pitting corrosion. The depth of the pits increased and new pits were formed until, after 126 days exposure, the entire surface was roughened and irregular.

Petroleum-Engineering Studies

Lake Creek Gas-Condensate Field, Tex.

The manuscript of the Lake Creek field study[1/] was completed in the fiscal year 1948 and published in November. The Lake Creek field, approximately 37 miles northwest of Houston, Tex., and 10 miles west of the Conroe oil field, is on the downthrow side of a pronounced fault, but the general structure is anticlinal. Condensate-bearing gas is produced from 22 multiple-completed wells that penetrate sandstone beds of the Wilcox group, Eocene age, between the depths of 8,820 and 11,840 feet. Each producing zone consists of one or more members composed of siliceous sandstone which locally are lenticular, and have a porosity ranging from 12 to 19 percent and permeability ranging from 6 to 23 millidarcys.

The relatively low permeability of the reservoir rocks was a controlling factor in the development and operation of the Lake Creek field, as indicated by the low initial daily rates of production of 0.62 to 4.7 million cubic feet of gas. Although the initial daily production was low, the high recoverable hydrocarbon-liquid content of the gas made development of the zones economically desirable.

Condensate-bearing gas, produced from the equivalent of 56 separate wells, is "cycled;" that is, it is passed through a plant where liquid products are extracted by reducing the pressure and temperature, and the dry residue gas is returned to the reservoir to maintain pressure and displace the remaining condensate-bearing gas. The gas-cycling plant was designed to process daily approximately 68.5 million cubic feet of wet gas and to return to the producing formations about 50 million cubic feet of processed gas at wellhead pressures of 4,040 to 4,050 psi. The average gas : liquid ratio was 7,067 cubic feet a barrel, and the hydrocarbon liquid content was 5.94 gallons per M cubic feet or 141 barrels per million cubic feet.

Many new types of packers, plugs, and complicated equipment were invented and developed to make dual and triple completions in the Lake Creek field safe, practical, and economical. The study of the Lake Creek field was begun originally at the request of the Petroleum Administration for War, and a restricted report was issued in October 1944. Through the cooperation of the operating companies, the report was brought up to date and published as a Bureau of Mines report of investigations.

Sheridan Gas-Condensate Field, Tex.

A petroleum-engineering study of the Sheridan field was begun at the request of the Petroleum Administration for War but was not completed before

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1/ Hill, H. B., and Vogel, Felix A., Jr., Petroleum-Engineering Study of the Lake Creek Field, Montgomery County, Tex.: Bureau of Mines Rept. of Investigations 4319, 1948, 65 pp.

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the end of World War II. Because of the general interest in deep-seated reservoirs containing condensate-bearing gas, Bureau of Mines engineers obtained permission and cooperation of the operators to continue the study and to publish the results.8/

The Sheridan gas-condensate field, Colorado County, Tex., is 85 miles southwest of Houston, and 115 miles east of San Antonio, Tex. Oil and gas reservoirs in this field lie on the downthrow side of a pronounced faulted zone consisting of a number of step faults or normal faults in echelon. A number of similar oil and gas fields that produce from the Wilcox group, Eocene age, have been discovered along this faulted zone which trends northeast-southwest from Newton County on the Texas-Louisiana line to Live Oak County in South Texas. The explored Wilcox section in the Sheridan field comprises four principal producing zones.

The producing strata in the reservoirs are relatively thin, tight, and lenticular, and the permeability is relatively low. The first three wells were completed in 1940 as oil-producing wells at depths of approximately 8,050 feet. Although the total thickness of the Wilcox section in the Sheridan field is unknown, the deepest well in the field was still in the Wilcox formation when drilling was stopped at a depth of 11,497 feet. Condensate-bearing gas from two zones discovered below the oil-bearing zones are being withdrawn and pass through a "gas-cycling" plant where the liquid products are extracted by reducing the pressure and temperature, and the dry gas is returned to the reservoirs to maintain pressure and displace the remaining condensate-bearing gas. The capacity of the plant which began operations in August 1945 is 100 million cubic feet of gas daily. The gas : liquid ratio of the gas processed during the first 14 months of operation was 15,764 cubic feet a barrel, with a hydrocarbon-liquid content of 2.66 gallons per M cubic feet or 63 barrels per million cubic feet of gas.

Carthage Field, Tex.

The engineering field study of the Carthage, Tex., field has been continued by maintaining to date all records of oil and gas production and new drilling. Since its discovery in 1936, the field has been developed so that, as of January 1, 1948, it covers a surface area approximately 30 miles long and 25 miles wide and includes 287 producing wells, of which 170 were dual completions producing from two separate reservoirs.

Reservoir engineers for years have had difficulty in making reliable estimates of the interstitial water content of petroleum reservoirs. Methods of obtaining cores of the reservoir rock have not been developed to the point where the cores retain representative amounts of the oil and water present in the reservoir when they are brought to the surface. In recent years research has developed a procedure known as the "restored-state method" whereby formation brine is reinjected into core specimens and then subjected to gas drive under controlled conditions. The brine retained in the core is determined, and this is considered to be the approximate amount of interstitial water

8/ Hill, H. B., and Vogel, Felix, Jr., Petroleum-Engineering Study of the Sheridan Field, Colorado County, Tex.: Bureau of Mines Report of Investigations 4367, 1949, 94 pp.

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present in the reservoir under original pressure and temperature conditions. During the past year, over 100 interstitial water determinations were made by Bureau of Mines laboratory technicians on core specimens obtained from productive wells in the Carthage field. The results indicate that interstitial water contents of 15 percent, 31 percent, and 10 percent will be used for the Hill, Upper Pettit, and Lower Pettit reservoirs, respectively, in estimating the recoverable reserves of gas and gas condensate. Although some engineers consider that the "restored-state method" gives more reliable estimates of interstitial water content of reservoir rocks than previously used methods, further research is needed to prove how much credence can be given the results obtained.

New Hope Field, Tex.

A petroleum-engineering study of the New Hope field, begun by Bureau of Mines engineers in 1945, is nearing completion. This field of 4,000 acres which overlies one limestone and three sandstone reservoirs at depths of about 8,000 feet and which has about 55 oil-producing wells, can be cited as one in which great effort is being made by the operators to apply modern engineering techniques to achieve more efficient recovery of oil.

The oil in the four reservoirs is undersaturated with gas, and the principal source of natural energy to drive the oil to the wells is derived from expansion of the reservoir fluids, although some effect of water encroachment has been observed. When the reservoir pressure in each of the four reservoirs declined rapidly and many wells ceased flowing, the operators began injecting water into the three uppermost reservoirs to arrest the decline of reservoir pressure. The relatively low permeability of the reservoir rocks requires extremely high injection pressures. The decline in reservoir pressure has been arrested in all three reservoirs, and an increase in reservoir pressure has been observed in two of them. The report will contain material-balance calculations and graphs demonstrating the beneficial effects of pressure maintenance by water injection. This report should serve as a guide to other operators, engineers, and geologists interested in similar reservoirs in which the principal sources of natural reservoir energy reside in the expansion of reservoir fluids.

Study of Reservoir-Oil Samples

North Lindsay Field, Okla.

The investigation of the producing characteristics of wells and the physical properties of the oil from the Bromide formation of the North Lindsay field in the southeastern part of the Anadarko Basin is a part of the Bureau's plan of studying important new oil fields. The study brought to light the unusual physical properties of the oil from this formation. Similar oils are being found at approximately the same depth in this general area. A report has been prepared for publication which presents data that are valuable in outlining the best production practice in obtaining maximum recovery of oil of the type found in the North Lindsay field.

Data resulting from the North Lindsay study will provide a basis for application of material-balance concepts to reservoirs containing similar

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oils. The ultimate quantities of oil recoverable by the usual pressure-decline production method of oil recoverable by pressure maintenance with gas injection and of oil recoverable by pressure maintenance with water injection may be estimated with more assurance.

The average depth of the midpoint of the Bromide sandstone reservoir is approximately 11,000 feet; the average thickness is 450 feet. Most of the reservoir rock is extremely hard and of low porosity and permeability. However, there are streaks of high porosity and permeability which permit a few of the wells to have high oil potentials.

Four wells were tested and sampled in an attempt to obtain a complete understanding of the physical properties of the reservoir oil. In testing the wells, gas : oil ratios were measured for several flow rates and for several operating pressures and temperatures of the gas-oil separator. Subsurface pressure and temperature measurements were made throughout the test. During the tests a sampler designed by Bureau engineers was lowered to a point near the bottom of the wells, where the instrument was closed, trapping a portion of the flowing fluid. The sampler permitted the oil to be brought to the surface without loss of solution gas. Duplicate subsurface oil samples were examined in the laboratory to determine solution gas : oil ratio, shrinkage in oil volume from the reservoir to the stock tank, density of solution gases, reservoir-oil viscosity at reservoir and lower pressures, and composition of reservoir oil and separator oil and gas. Special experiments were made to determine the operating pressure of a field gas-oil separator for maximum oil recovery and the volume of additional oil recovered by two-stage separation over that recovered by the customary single stage.

Flow-test results on two wells (tests 1 and 4) presented in table 1 show that the gas : oil ratio decreased as flow rates increased, indicating that gas originally not in solution with the oil came into the well bore during low rates of flow. Test 2 shows that reducing the separator temperature from 64° to 44° F. decreased the gas : oil ratio from 2,502 to 2,404 cubic feet per barrel at 60° F. In test 3 the gas : oil ratio was reduced from 2,850 to 2,570 cubic feet per barrel by changing from single to two-stage separation with the first separator at 500 and the second at 63 psi. The experiments indicated that a decrease in separator temperature would increase the oil recovery 2 percent, while addition of the second separator would increase recovery 6 percent.

The physical properties of the reservoir oil as determined by the laboratory study of the subsurface samples follow:

1. The gravity of the stock-tank oil is high, approximately 46° A.P.I.;
2. The solution gas : oil ratio of the initial reservoir oil was higher than that of any other known oil in Oklahoma reservoirs - approximately 2,500 cubic feet per barrel by the flash gas-liberation method;
3. More than 2 barrels of the initial reservoir oil must be produced to yield 1 barrel of oil in the stock tank;
4. The gas liberated from the oil in the reservoir at approximately initial reservoir pressure had a specific gravity of 0.83 (air = 1.0), and the mole percent of butanes and heavier in the gas was 8.6;

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5. The density of the initial reservoir oil was 0.49 gram per cubic centimeter or 30.6 pounds per cubic foot;
6. The viscosity of the initial reservoir oil was 0.16 centipoise, which is less than that of water (0.33 centipoise) both at reservoir temperature, 189° F.

TABLE 1. - Flow-test data, North Lindsay field, McClain County, Okla.

Date	Choke size, inches	Subsurface pressure at -9,900 ft., psi	Separator Press., psi	Separator Temp., °F.	Sp. gr. sepr. gas, air = 1.0	Oil prod. rate, bbl./day	Gas:oil ratio cu.ft./bbl. (14.4 psia and 60° F.)
			Lawson B well No. 1				
			TEST 1				
10-29-46							
10-30-46	6/64	4,836	47	60	-	88.4	2,588
10-31-46							
11- 1-46	8/64	4,835	47	60	0.741	173.7	2,434
11- 2-46							
11- 3-46	10/64	4,804	47	60	-	267.2	2,320
			TEST 2				
4-27-47							
4-29-47	9/64	4,535	52	64	0.756	217.3	2,502
5- 1-47							
5- 4-47	9/64	-	52	44	.685	216.2	2,404
			TEST 3				
11- 2-47							
11- 4-47	11/64	4,240	63	60	0.756	303.9	2,850
11- 5-47			1/ 63 &				
11- 6-47	11/64	-	500	60	2/ .697	318.1	2/ 2,570
			Robinson well No. 1				
			TEST 4				
4-29-47			1/ 50 &				
5- 1-47	8/64	4,286	500	65	2/ 0.699	71.7	2/ 5,120
5- 2-47			1/ 53 &				
5- 3-47	10/64	4,250	500	60	2/ .680	244.8	2/ 3,640
5- 4-47			1/ 55 &				
5- 5-47	14/64	4,172	550	50	2/ .680	503.9	2/ 3,025

1/ Two gas-oil separators in series.
2/ Combined gas from both the high- and low-pressure separators.

Relatively few known reservoirs contain oil with a viscosity lower than that of water. A water flood (natural or through water injection) in a reservoir containing oil of the low-viscosity type found in North Lindsay might sweep a larger portion of the reservoir, other factors being equal, than would occur in reservoirs containing normal to high viscosity oils. In a reservoir with the oil viscosity lower than water, the volume of fluid flowing through the more permeable section probably would not increase and possibly would decrease as the water "fingered" out into the reservoir or broke through to producing wells. Thus, when considering only viscosity, one would expect a more uniform water front when the viscosity of the reservoir oil was less than that of water.

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Elk Basin Field, Wyo. and Mont.

A report covering the results of studies made during 1943 to 1945 of the reservoir-oil characteristics in the Elk Basin, Wyo. and Mont., Tensleep-sand reservoir was prepared for future publication. The studies upon which this report is based show that the oil-gas solution in this reservoir varies greatly in its characteristics depending on location in the reservoir, a variation far exceeding anything that had been thought to exist within an oil reservoir heretofore. The oil had a saturation pressure of 1250 psia (pounds per square inch absolute) and had 480 cubic feet of gas in solution per barrel at the crest of the reservoir. These values decreased uniformly to a saturation pressure of only 540 psia and 140 cubic feet of gas a barrel as the subsurface oil-gas solutions were sampled progressively farther down the flanks of the structure to the oil-water zone. The values of reservoir oil shrinkage when the oil was produced also decreased in the same manner. The hydrogen sulfide content of the solution gas also decreased from 18 percent at the crest to 5 percent at the edge.

Rangely Field, Colo.

Research regarding the characteristics of the Weber-sand reservoir oil in the Rangely field was continued at Rangely and the Laramie Station. All the needed data have been acquired and are being compiled, studied, and prepared for a report on this large reservoir. It has been determined that the oil in the Weber reservoir has characteristics that vary considerably, depending upon its location in the reservoir. The variation of these characteristics is more unusual than that found in the Elk Basin field, for in the Rangely field the oil in the crest of the reservoir is saturated with gas at reservoir conditions and decreases in saturation pressure and amount of gas in solution in it much in the same manner as the oil in the Elk Basin field.

Well-Spacing Studies

Data pertaining to the relation between ultimate oil recovery and well spacing in more than one hundred oil fields throughout the United States are being subjected to continual study by the Bureau of Mines engineers at the San Francisco Petroleum Field Office, and during the past year limestone reservoirs have received special attention. In general, it may now be stated tentatively, but only on a qualitative basis, that ultimate oil recoveries from limestone reservoirs increase with shorter distances between wells and with increases in the A.P.I. gravity of the produced oil. This tentative conclusion was drawn previously with respect to sand and sandstone reservoirs, and field investigations made during the past year, therefore, appear to support the conclusion regardless of the composition of the oil-reservoir rock.

Theoretical work by Bureau of Mines engineers assigned to the well-spacing problem includes a comprehensive analysis of multiphase fluid flow through oil-reservoir rocks. Work on this study is now under way, and the purpose is to search for methods whereby the well-spacing problem may be investigated by applying the basic principles of fluid mechanics and thermodynamics to the flow of petroleum-reservoir fluids (oil, gas, and water) through porous reservoir rocks to wells.

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It is expected that the foregoing field investigations and theoretical studies will lead to or at least suggest laboratory experimentation that should be conducted to substantiate conclusions that may be based solely on mathematical and physical reasoning or on incomplete field data. With this point of view in mind and with some tentative conclusions regarding well spacing already drawn, Bureau of Mines engineers are currently planning initial laboratory experiments to serve this purpose.

Drilling-Fluid Research

Rotary-Tool Coring

As sound engineering programs for efficient exploitation and production of oil and gas fields must be based on accurate knowledge of the properties of the petroleum-bearing reservoirs, a series of tests is being carried out in cooperation with the Special Study Committee on Well Spacing and Allocation of Production of the American Petroleum Institute and several oil companies to develop improved methods for measuring the quantities of oil, gas, and water in porous petroleum-bearing reservoir rocks.

In one of the early tests an effort was made to obtain uncontaminated cores in a Texas field, using a pressure core barrel with an oil-base drilling-fluid having very low rates of filtration as measured by the standard drilling fluid filter test. An organic chloride tracer soluble in oil, insoluble in water, unaffected by bacteria, and extremely stable at high temperatures was added to the drilling fluid to provide a means for quantitatively measuring the contamination of the cores by filtrate (oil) from the oil-base drilling fluid. Because very little oil sand was penetrated in coring the well and the performance of the pressure core barrel was not entirely satisfactory, the test did not yield the information sought. The test indicated, however, that even with a pressure core barrel formation cores are flushed to some degree by the drilling fluid and that they provide little, if any, more information regarding the fluids in the reservoir than is obtained from cores taken with conventional core barrels.

In subsequent tests made in the South Coles Levee field, Calif., and in a well in the Rangely field, Colo., conventional-type core barrels were used, with oil-base drilling fluid containing the same organic chloride tracer in the earlier test. The primary purpose of the tests was to determine if uncontaminated cores could be obtained in fields where reservoir pressures are high with conventional-type core barrels using an oil-base drilling fluid having very low rates of filtration as the circulating medium in the borehole.

The results of the tests indicate that nearly all of the cores contained filtrate from the drilling fluid, which apparently altered the oil content of the cores but did not affect their water content. Therefore, as the oil content of cores cut from zones known to contain no free gas equals the total pore volume less the pore volume filled with interstitial water, the analysis of cores cut with an oil-base drilling fluid in the hole penetrating a zone containing no free gas and from which no water is produced yields reliable data concerning the oil and water content of the producing formation.

In another series of tests conducted in a Gulf coast oil field, cores were cut by the operating company with a conventional-type core barrel with

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an oil-base drilling fluid containing an organic chloride tracer in the bore hole. These cores are being used to determine quantitatively the volume of filtrate (oil) that enters them from the drilling fluid. When the results of this series of tests are completely analyzed the contaminating effect of the oil-base drilling fluids on the results of the core analysis can be evaluated.

Cable-Tool Coring with Oil-Base Drilling Fluids

Reservoir pressures and temperatures were relatively high in the Gulf coast, Rangely, and South Coles Levee tests. To determine if uncontaminated cores can be obtained from formations under lower pressure and temperature, similar tests using an oil-base drilling fluid with a tracer now are in progress in wells drilled in the Appalachian area where cores customarily have been cut by cable tools with water in the boreholes. These tests are being carried out in cooperation with a number of eastern oil producers by the Bureau of Mines Petroleum Field Offices at Franklin, Pa., and at San Francisco, Calif.

Most of the cores procured in the Appalachian region are drilled with cable tools, using fresh water as the drilling fluid. Ordinarily laboratory analyses of these cores show lower oil content and higher water content than is considered representative of reservoir conditions as is often proved later by oil-production operations.

Owing to the vital importance of knowing the true oil and water contents of reservoirs in secondary-recovery developments in the Appalachian region, Bureau engineers have conducted field and laboratory investigations in efforts to apply oil-base mud to cable-tool coring, with the hope that the resulting data would depict reservoir conditions more nearly. A specially compounded oil-base mud was procured for the tests and used in coring six wells this year - one in New York, three in Pennsylvania, and two in West Virginia. Anticipating invasion of the core specimens by the oil component of the oil-base mud, an organic chloride compound, soluble in oil but not in water, was added as a tracer to the mud on each coring test.

The oil-base mud coring tests were not entirely satisfactory. It was proved, however, that cable coring tools would operate satisfactorily when oil-base mud is used as the drilling fluid. The interstitial oil-content data obtained by analyzing the cores were unsatisfactory because of troubles resulting from the tracer employed. The water-content data, however, were very promising; and, when compared with connate-water-determination data, they appeared to be approximately representative of reservoir conditions. Further research using a different tracer should improve the value of the oil-content data.

Productivity of High-Pressure Gas Wells

The study of the productivity of high-pressure gas wells was undertaken in July 1947 as an outgrowth of the problem of gas-well gaging. The results of the study of gas-well gaging by Rawlins and Schellhardt[9/] were published in

9/ Rawlins, E. L., and Schellhardt, M. A., Back-Pressure Data on Natural-Gas Wells and Their Application to Production Practices: Bureau of Mines Mon. 7, 1935, 210 pp.

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1935. Since then, the drilling of wells to deeper and deeper horizons led to discovery of natural-gas reservoirs with increasingly higher pressures and temperatures. Both pressure and temperature have marked influence on the volume of liquid hydrocarbons in the flow string of producing gas wells, as well as on other characteristics of the gas, such as compressibility and viscosity. Accurate measurements of the productivity are difficult when gas wells produce through long strings of pipe with hydrocarbon-liquid condensation and wide temperature changes within the well.

A survey was made to determine the specific problems in well testing on which experimental data were needed. The difficulties seemed to be in the methods of obtaining test data rather than in the basic theory behind the back-pressure method of well testing. The main points on which more data are needed which the survey brought to light are:

1. The temperature of both flowing and static gas columns and the temperature changes that occur when a well is started to flow.
2. The specific gravity of the gas within the well and the related problems of compressibility and liquid condensation in the well.
3. The pressure loss due to friction in all types of well flow strings.
4. The pressure loss across bottom-hole and side-door chokes frequently used in gas wells.
5. The criteria for indicating proper flow stabilization for testing.

In view of the extensive research now being done on the pressure loss due to friction in horizontal natural-gas pipe lines, it was decided to conduct experiments on gas wells to find if gas wells behaved like pipe lines. To this end, two wells with tubing were selected for study of flow through the annular space between the casing and tubing, and two wells without tubing were selected for study of flow through casing alone. To simplify the problem by eliminating as far as possible wide temperature changes, large compressibility effects, and phase changes, relatively shallow, dry gas wells in the Panhandle area of Texas were selected for the study.

In testing the untubed wells, surface pressures were measured with a calibrated piston gage, while pressures at the bottom of the wells were measured with a subsurface pressure recording gage. Flow rates from 5 to 18 million cubic feet of gas per 24 hours were measured with orifice meters and a critical flow prover. The experimental results, expressed as friction factors (square root of the reciprocal of the Fanning friction coefficient), for the well with 5.012-inch inside-diameter casing ranged from 14.8 to 16.8, which indicates that flow in untubed wells is similar to that for horizontal pipe lines.

In the study of annular flow, the difference in pressure between the flowing column and the shut-in column was measured with the differential part of an orifice meter. Thus the pressure loss due to friction was measured to about 0.5 inch of water. Subsurface pressures were calculated on the shut-in

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gas column to the highest opening between the tubing and the annulus. Values of the friction factor for flow rates near 5 million cubic feet of gas per 24 hours were between 11.8 and 12.6 for flow in two different-size annular spaces.

Calibration of Subsurface-Pressure Instruments

Successful determination of the pressure loss due to friction in untubed gas wells requires accurate measurements of subsurface pressure. To fulfill this requirement, an extensive study was made of the characteristics of a 1,200-psi range, Amerada-type, subsurface pressure gage. The investigation led to the identification and the determination of the magnitude of eight sources of error that may cause erroneous results in gage calibration and usage.

Pressure deflections recorded by the gage and corresponding calibration pressures at four calibration temperatures were fitted by the method of least squares to linear equations. The slope of the line is the modulus and the intercept of the line on the pressure axis is the zero-pressure correction where deflection is zero. The zero-pressure correction may have either positive or negative values.

In all, 237 calibration points were examined for the instrument. The sum of the deviations without regard to plus or minus signs between the pressure applied to the gage and pressure indicated by the least-square lines was 69.2, or the arithmetic average was 0.29 psi. The largest deviation observed was -1.0 psi.

The eight sources of error that may enter into the calibration and use of a subsurface pressure gage are: (1) Inability to reproduce gage measurements, (2) change of gage characteristics with time, (3) a need for improved charts and stylus points, (4) pressure shocks transmitted to gage from pump during calibration, (5) failure to reach temperature equilibrium within the gage, (6) failure to reach mechanical equilibrium within the gage, (7) effect of pressure on the outside of the pressure element, and (8) change of zero-pressure correction with temperature.

The various sources of error affect the accuracy of the gage recordings to varying degrees. For example, subsurface-pressure measurements were reproduced on three successive traverses in a flowing gas well with a maximum variation of 0.7 psi. In comparison, a zero-pressure line placed on the gage at 60° F. differs from one at 120° F. by a distance equivalent to 2.5 psi for the 1,200-psi gage, and errors of this or greater magnitude may be obtained in field practice when the influence of temperature on the position of the zero pressure line is ignored.

SECONDARY RECOVERY

The high demand for petroleum and its products and the steadily increasing cost of discovering and developing new oil fields emphasize the importance of recovering the most oil possible from known fields. Secondary-recovery methods, which increase oil recovery by the injection of water, natural gas, or air into partly depleted petroleum reservoirs, therefore, are becoming increasingly important in the national petroleum economy.

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Until recently the application of secondary-recovery methods of oil production was almost the exclusive field of individuals and small companies having low overhead costs. During the past year, however, several large oil companies, cognizant of the need for greater recovery from known reserves, have established secondary-recovery divisions and have entered water-flooding operations. The possibility of water-flooding sands at depths to 4,000 feet below the surface now is being tested by experimental projects. The results of these trial floods will point the way to development of large areas for secondary-recovery operations.

The increased importance of stimulative methods of oil production was evidenced during the year by the formation, within the Interstate Oil Compact Commission, of a Secondary-Recovery Division, with aims as follows:

1. To encourage legislation permitting secondary recovery and the unitization of oil fields to permit effective application of secondary-recovery methods, pressure maintenance, and cycling.

2. The collection of statistical information on secondary-recovery operations throughout the United States and the study of the secondary possibilities of all oil fields to permit better evaluation of the secondary reserves of the United States.

3. The encouragement of research by States on methods for increasing oil recovery and a periodic review of oil-recovery research in progress throughout the United States.

4. Maintenance of contacts with Federal agencies having relations of various kinds with the oil and gas industry.

5. Coordination with other organizations having interest in secondary-recovery work.

A Secondary-Recovery Advisory Committee, composed of outstanding authorities in the petroleum industry, was appointed by the Interstate Oil Compact Commission to direct the work of the newly organized division. The Bureau of Mines is represented on this committee and through it has been active in coordinating and directing the activities of the division.

The role of the Bureau of Mines in promoting and encouraging oil conservation through the application of improved secondary-recovery methods recently was brought into sharp national focus by passage of the Synthetic Liquid Fuels Extension Act, which provided a sum not to exceed $1,000,000 for a program of production research on secondary recovery from stripper oil fields and in refining processes. The expanded program of secondary-recovery research was the subject of a conference by representatives of all the stations and field offices of the Petroleum and Natural-Gas Branch of the Bureau of Mines. A carefully coordinated program, designed to meet the most urgent needs of every section of the Country was developed, and active work will be initiated immediately.

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Methods of Increasing the Recovery of Oil

Field Studies

Through study and research the Bureau of Mines has, for more than 30 years, been engaged in a program devoted to increasing oil recovery from reservoir rocks. Important parts of this program are the engineering studies of petroleum reservoirs suitable for the application of secondary-recovery methods and the study of oil fields, or areas, in which secondary-recovery methods have been applied. The former provide information that will make possible more intelligent application of secondary-recovery methods to the particular reservoirs concerned, whereas the latter serve as a "yardstick" in applying these methods to similar fields.

Atlanta Field, Ark.

A recently completed engineering field study[10/] explains how modern efficient methods of oil production are being employed in the Atlanta oil field of Columbia County, Ark., to increase the recovery of oil from oolitic limestones of the Smackover formation. The report describes the reservoir conditions and production history of the field from its discovery in 1938 to July 1, 1947.

In the Atlanta field the Smackover limestone is folded into an east-west anticline about 7 miles long, and oil and gas have accumulated above water in the porous oolitic limestone at the top of the structure. The oil-productive area includes 4,172 acres; and the maximum thickness of the reservoir rock, above the oil-water contact, is about 45 feet. The porosity of the oil-bearing zone varies widely between wells and between zones in the same well, but the weighted average for the entire field is about 15 percent. Connate water, as determined by the restored-state method, filled 26 percent of the pore space in the oil reservoir and 25 percent of the pore space in the gas cap of the western part of the field. The pore spaces of the reservoir rock originally contained about 24 million barrels of "stock-tank" oil and 15 billion cubic feet of gas.

To promote efficient use of reservoir energy, the rate of oil production and the relative volumes of gas and water produced with the oil are regulated by the Arkansas Oil and Gas Commission. Wells are cased and cemented through an upper gas sand, and oil production is obtained through perforations opposite oil-saturated sands below. A water drive is active along the north and south edges of the field, and several wells in these areas have been abandoned because of water incursion. By comparing the calculated volume of recoverable oil originally present in these water-swept areas to the volume actually produced from the wells, the efficiency of the natural water drive in the Atlanta field is shown to approximate 72 percent.

10/ Riggs, C. H., Petroleum Engineering Study of the Atlanta Oil Field, Columbia County, Ark.: Bureau of Mines Rept. of Investigations 4455 (in press).

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Since August 1946 the brine produced with the oil, augmented by extraneous fresh water, has been injected into the producing formation through an input well on the southeast edge of the field. During the first half of 1947, the volume of water thus injected exceeded the volume of water produced from the field. This has resulted in a conservation of reservoir energy, as indicated by the production of more oil per unit of pressure drop than during the earlier life of the field. The report indicates that the injection of water at a greater rate and through several properly located wells would stabilize the reservoir pressure and further increase the recovery of oil.

Weber Pool, Okla.

Field studies that review the production history, provide a complete reservoir analysis, and set forth the oil reserves available from the field by modern water-flooding practices are a definite aid to oil operators. The Weber oil pool in the Bartlesville-Dewey field, Washington County, Okla., now being studied by Bureau engineers, is an area where water flooding will be practical and profitable. This field was discovered in 1905 and developed between 1906 and 1908. It includes approximately 2,700 productive acres on which nearly 700 producing wells were drilled to the Bartlesville sandstone. Initially many of the wells produced at the rate of 500 or more barrels daily, but by 1948 oil production from the old wells averaged only 2 barrels daily. During the past year, 12 oil wells were drilled and completed in the Bartlesville sandstone with initial producing rates averaging 12 barrels daily. Three of these wells were cored, and the core analyses were available for studies of the porosity, permeability, the present oil saturation of the producing formation and the original connate-water saturation.

A study of all available cores and well logs shows that the Bartlesville sand in the Weber pool lies in a small syncline at the extreme north end of the Bartlesville anticline. The upper part of the Bartlesville is a gas sand, irregular in occurrence, and, where present, the thickness ranges from less than 1 foot to about 40 feet. Thickness of the oil producing portion of the sand averages about 45 feet, with a maximum thickness of about 80 feet in the southern part of the pool. Air and gas injection have been tried in some areas of the Weber pool, but water flooding has not been attempted. However, preparations are under way to develop a small flood in the central part of the field.

West Red River Field, Okla.

The West Red River field, Tillman County, Okla., is approximately 8 miles northwest of Burkburnett, Tex., and the wells in the field are in the bed of the Red River between the medial line and the south bank of the river. Both Oklahoma and Texas claimed ownership to the land overlying the oil field when the field was discovered, and the field was operated by a receiver from April 1920 to July 1924 while the case was on appeal to the United States Supreme Court. Operations were transferred to the Secretary of the Interior as trustee July 1, 1924, who in turn directed the Bureau of Mines to operate the field until all claims were adjudicated, leases granted, and the properties returned to the owners. Supervision by the Bureau of Mines ended December 1, 1925, but subsequently the Geological Survey was assigned supervision because the land between the medial line and the south bank of the Red River was declared to be public domain.

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During the period of litigation separate accounts of production, receipts, and disbursements were kept on each well; and these records, over a period of 5 years, are particularly interesting because they show the progress made in petroleum-production techniques during the past 26 years. These data and subsequent records were used in studying the field and preparing a report.

The primary objectives of the report[11] are: To discuss the surface hazards of development in a river-bed field; to interpret the reservoir conditions; to discuss subsurface problems; and to record the production history of a lenticular sandstone reservoir in which the productivity of the wells probably results from local sand conditions rather than structure, and in which the principal source of energy was dissolved gas. The West Red River field delimited an area of about 327 acres, and the depth of the wells ranged from 1,550 to 1,600 feet. Methods of stimulating the production of oil included shooting with explosives, cleaning out, applying vacuum, and repressuring with air and gas.

The total production of oil from Government-operated leases considered in this study was 6,900,440 barrels up to January 1, 1947, from 81 oil-producing wells, 10 gas-input wells, and 5 nonproducers. The daily oil production after 26 years is approximately 170 barrels and a maximum of 260 barrels of water from 43 wells. The estimated recovery thus far has been 603 barrels of oil per acre-foot of reservoir sandstone. The results of the study should be particularly helpful to petroleum engineers investigating the possibilities of secondary recovery in similar reservoirs.

Boggs Field, W. Va.

Engineers of the Franklin office completed a study of the Boggs field, Roane County, W. Va., during the fiscal year 1948. The report[12] gives an engineering appraisal of the field, its development and operation from date of discovery to date of probable abandonment, estimates of the quantity of oil remaining in the sand and the probable total volume of oil to be recovered. Surface maps of the properties and isopachous and contour maps of the sand are presented.

The engineering analysis shows that the cumulative oil produced in 15 years of primary-recovery operation amounted to only 8.54 percent of the original oil in place; that during both primary recovery and 19.5 years of secondary-recovery gas-drive operations, 13.28 percent of the original oil was produced and that with 22 additional years of operation, using the same production techniques, the total volume of recovered oil will amount to only 15.25 percent of the crude oil originally in the reservoir.

11/ Hill, H. B., Johnston, Kenneth H., Coleman, T. L., and Seward, J. M., Petroleum-Engineering Study of the West Red River Field, Tillman County, Okla: Bureau of Mines Rept. of Investigations 4450, 1949, 97 pp.

12/ Tignor, E. M., Jennings, Thomas, and Krause, Leon, Secondary Recovery of Oil by Gas Injection in the Boggs Field, Roane County, W. Va.: Bureau of Mines Rept. of Investigations 4430, 1949, (in press), 31 pp.

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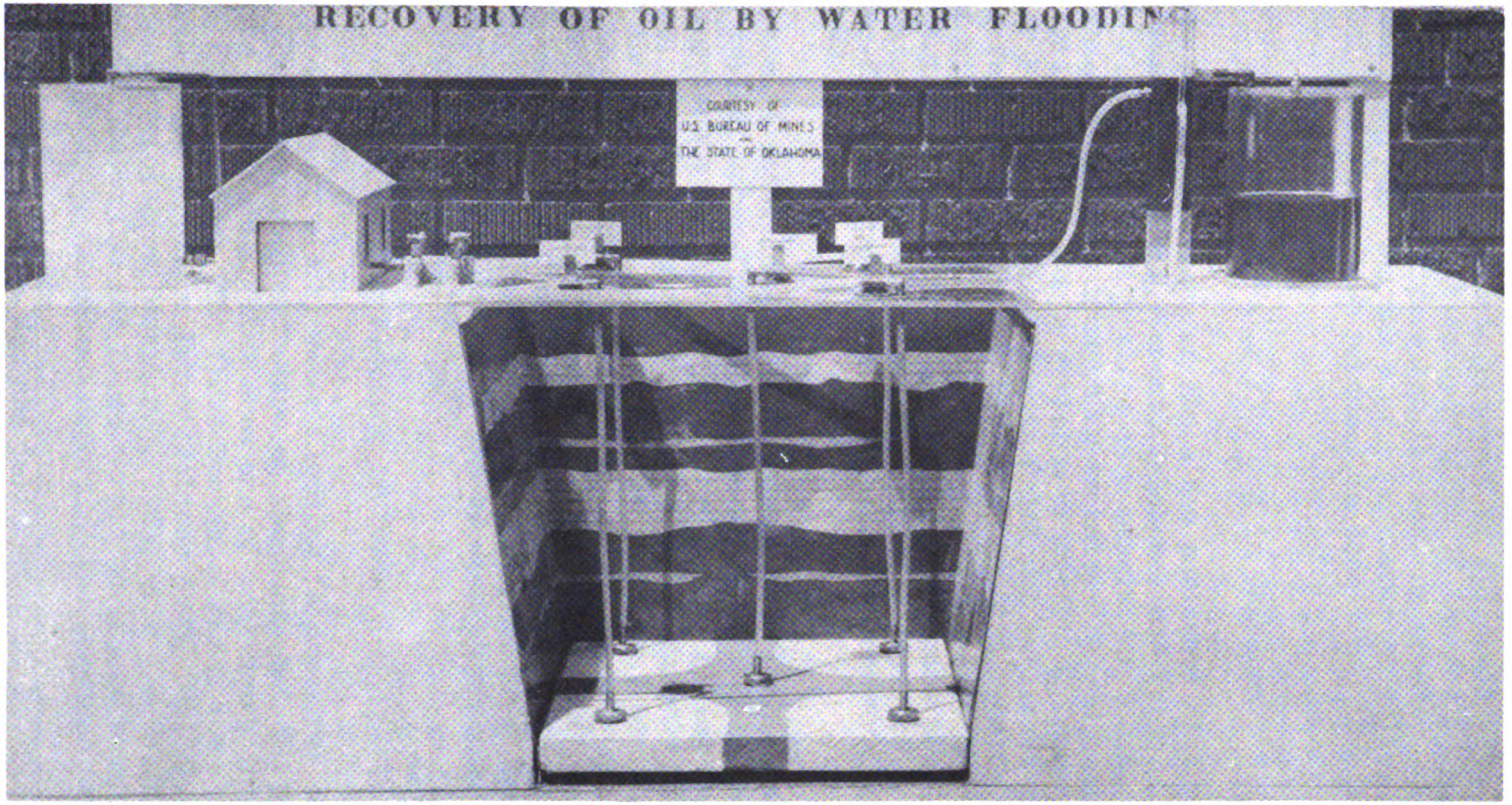

Figure 5. - Model to demonstrate recovery of oil by water-flooding.

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This report significantly points out the need for unitization of leases, particularly in the Appalachian region, where secondary recovery must be relied upon to exploit stripper-oil properties to obtain the greatest ultimate recovery. Even with the Boggs field operated as it was during the primary-recovery period, a greater ultimate recovery of oil could have been realized by secondary-recovery gas-injection operations if the field had been operated under proved unitization principles and the same or greater volumes of gas injected into the reservoir through a greater number of wells. Furthermore, the recovered oil would have been produced in less time, thus lowering the production cost.

History of Water Flooding in Oklahoma

In previous years the Bureau of Mines has published histories of water-flooding operations in Illinois, Kansas, Oklahoma, and Texas. Because of the increased water-flooding activity there is a persistent demand from the oil industry that these reports be brought up to date. Bureau engineers are engaged in assimilating data for a revision of Report of Investigations 3728, History of Water Flooding of Oil Sands in Oklahoma, published in 1942. Data assembled indicate that 63 operators have been granted permits to water-flood 40,420 acres of oil lands in 17 counties of Oklahoma. The increased importance of secondary-recovery production methods in meeting the demand for petroleum products is evidenced by the fact that 12 major oil companies are engaged in water-flooding operations in Oklahoma, as compared to 6 such companies in 1942.

Figure 5 shows a model constructed to demonstrate the method and equipment used in a typical water-flooding project. The stone in the lower center of the figure represents the oil reservoir and the overlying layers of limestone, sandstone, and shale penetrated by the wells (plastic tubing) are represented on the background. The water-treating plant and injection equipment are shown at the left of the model and the gun barrel and oil-storage tank at the right. The model represents a typical five-spot pattern with water-injection wells at the four corners of a square and an oil-producing well in the center. The advance of the water from the four injection wells toward the producing well in the center can be seen through the transparent plastic coating on the "reservoir" rock.

Water Flooding in Texas

Secondary recovery of oil by water flooding is practiced more extensively in North Texas than in any other section of the State and the progress and experience of the operations in that area are of continuing interest to all branches of the oil industry. The first Bureau of Mines report on water flooding in North Texas (Rept. of Investigations 3906, published in 1946) chronicled the activities from December 7, 1935, when the Railroad Commission of Texas granted The Texas Co. the first permit to inject water into an oil-bearing sand, through 1944. A second report[13] was prepared as a supplement

13/ Guthrie, R. K., Amyx, James W., and Taliaferro, D. B., Secondary Recovery of Oil by Water-Flooding in Fields of North Texas (Suppl. to Rept. of Investigations 3906): Bureau of Mines Rept. of Investigations 4250; 1948, 158 pp.

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to Report of Investigations 3906 to show the progress and expansion of water-flooding operations and technique in North Texas through 1945, 1946, and into 1947. The two reports are to be considered as companion publications.

The report issued in February 1948 summarized the pertinent data on 57 water-flooding projects in North Texas, an increase of 18 over the number of projects reported in 1946 (Rept. of Investigations 3906). The results obtained in each water-flooding project were analyzed to point out the probable causes of success or failure of the projects. In October 1947, 5.4 million barrels of oil was produced in the North Texas area, and 0.87 percent of that amount was recovered from leases on which water-flooding operations were in progress.

Secondary recovery by water flooding has been undertaken in four major oil-producing areas of Texas: North Texas, South Texas, the Panhandle, and East Texas. Excepting the North Texas area, these water-flooding activities are in the pilot or experimental stage. Another report[14/] was prepared to give a resumé of water-flooding developments in the North Texas area and to present only factual data pertaining to the few projects in the other parts of the State. The scope of this paper is limited to those projects in which water is being injected into oil-bearing reservoirs that have been depleted of their natural energy and in which no effective natural water drive has been recognized. Pressure-maintenance and brine-disposal projects were not included in this report.

Conditioning Water for Subsurface Injection

The treatment and conditioning of injection water to prevent plugging of the sand and corrosion of equipment is vitally important in water-flooding operations. To obtain data on treating methods and their results, the Bureau of Mines acquired and equipped a mobile water laboratory, and tests of injected water were made on 10 water-flooding projects in Kansas and Texas. The water was sampled at several points during treatment and before injection, and tests were made to determine hydrogen-ion concentration, alkalinity, carbonate stability, dissolved gases, and dissolved and total iron content. Special 72-hour tests were made to determine the corrosiveness of metal disks. All water samples were microscopically examined for algae and other organic matter. These tests showed that, at several plants, the treatment was ineffective or incomplete, and as a result of the tests some of the operators have made improvements in the equipment or method of water treating.

Input Rates and Pressures for Water-Flooding Oil Sands

When water is injected into oil producing formations at successively increasing sand-face pressures, a critical input pressure is finally reached which ruptures the formation so that injected water channels directly to producing wells without displacing oil into them. Knowledge of the pressure at which this channeling will occur is important for efficient water-flooding operations. To learn more about pressures and rates, Bureau of Mines engineers

14/ Guthrie, R. K., and Amyx, James W., Water Flooding in Texas: Chapter in the forthcoming revised edition of the American Petroleum Institute volume, Secondary Recovery in the United States.

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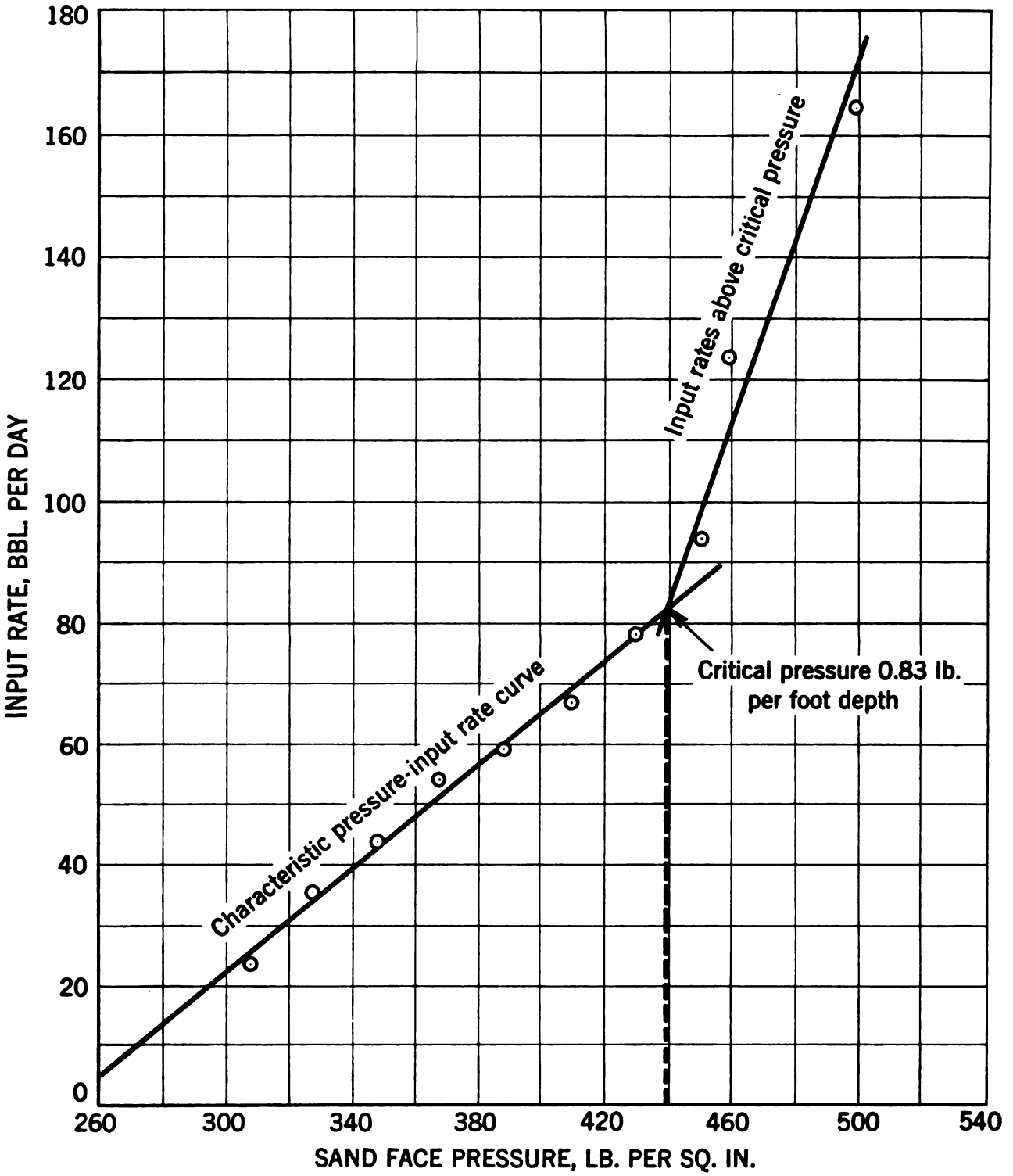

Figure 6. - Relationship of well-head pressure to injection rate on a typical water-input well.

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have made a series of water injectivity tests in several fields in Kansas, Oklahoma, and Texas. From a series of such tests on each well, data are accumulated to show the characteristic pressure-input-rate curve, and the critical pressure above which the injectivity rate increased disproportionately. Rates and pressures for a representative input well in the Isenhower field in Texas are shown in figure 6. At sand face pressures between 260 and 439 psi, the rate at which the Lower Cook sand, at a depth of 528 feet, took water was directly proportional to the pressure; about 0.0353 barrel per day per foot of sand for each pound of increased pressure. Above a critical pressure of 439 psi, equivalent to 0.83 pound per square inch per foot of depth of the sand, there was a marked increase in the injectivity rate for each pressure increment. Tests on other wells in Kansas, Oklahoma, and Texas indicate wide variation in critical pressures, from 0.7 psi per foot of depth for the Gunsight sand in Texas to 1.4 psi per foot of depth for the Squirrel sand in Kansas. At pressures below the critical, the input rate per foot of sand ranged from 0.005 barrel per day per pound of pressure for the Squirrel sand to 0.076 barrel per day for the highly permeable Stein sand in Texas.

Selective Plugging

For efficient and profitable secondary-recovery operations, the injected fluid must enter and displace oil from productive zones and be excluded from those open or depleted zones which would permit the fluid to channel directly to the producing wells. Recently, the Bureau of Mines has initiated a study to determine the position of these open zones and to develop methods of selectively plugging them. A fluid-level indicator to locate the top of a column of water being displaced by air into the producing formation has been developed, and successful trial tests were made in two wells. At a constant sand-face injection pressure, the rate of liquid-level drop is a function of the intake capacity of the water-covered sand and of the volume of water in the hole. The fluid-level gage measures the rate of drop in liquid level, and a well caliper is being constructed that will measure the diameter and volume of each foot of open hole and thus more accurately determine the volume of liquid entering each foot of sand as the level is depressed.

Laboratory tests indicated that an asphalt emulsion might be successfully used as a plugging material, and field tests on two wells have shown good results. Selective plugging operations in which a commercial resinous powder emulsion was used, were witnessed and results were noted.

Flowing Oil Wells on Gas-Injection Projects

Progress was made on an investigation, under way for several years, to determine the fundamental characteristics of flowing the oil produced from marginal wells on air-gas injection projects through small-diameter siphon-type flow strings. The initial objective was to determine if the very small quantities of oil accompanying the injected gas to the producing well bores could be flowed intermittently rather than pumped intermittently, thus utilizing the energy remaining in the injected gas after passage through the sand from injection wells to producing wells to lift the oil production by siphon flowing to the surface and into tankage. Following some experimentation in the field, the technique proved feasible in wells 300 to 1,100 feet

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deep. Flowing of this type has not been tried in deeper wells. After several years of development through laboratory and applied field research, the flowing of marginal oil wells in the vicinity of Oil City, Pa., is considered an improved oil-production technique and is practiced where reservoir conditions permit. The practice probably will be greatly extended when 1-inch-diameter pipe and other oil country equipment become more plentiful.

To make the flowing of small marginal wells on gas-injection projects successful and profitable, operators have found it necessary to improve many operating practices. In some reservoirs, higher gas-injection pressures and higher gas-injection rates, under precise control, are required to make the wells flow properly. The factors affecting the design of flow-string siphons of small diameter (1 inch) have been investigated in the laboratory and the results promptly applied in the field.

On July 1, 1948, 170 flowing oil wells, on 17 leases operated by 7 companies were equipped with flow strings designed by Bureau engineers. Of the 170 flowing wells, 130 are being operated in one small area near Oil City, 78 being operated on one lease.

Rehabilitation of Stripper Oil Wells

The future of oil fields in the Appalachian region, particularly southwestward from Pittsburgh, Pa., depends directly on the maintenance of existing wells. These fields, drilled many years ago, have been depleted of the major part of the original oil-driving gas energy, but enormous quantitites of crude oil remain in the reservoirs, awaiting extraction by secondary-recovery methods. Although the gas originally stored with the oil in these reservoirs has been produced faster than the associated oil, many fields still contain enough gas energy to drive large quantities of oil to the wells at a profitable rate if the oil can get into the well bore and be pumped into stock tanks at the surface. Unfortunately, however, the age of most of these wells greatly exceeds the useful life of the original equipment. Where the original equipment or replacement equipment has not been maintained, oil-production costs have gradually approached the income derived from the sale of oil. Furthermore, dilapidated well equipment and the old practice of leaving much of the hole uncased have caused the wells to cave, aggravated by water leaking into the wells from upper formations through corroded casing. These cavings, mixed with the water and wax accumulated for many years, have effectively sealed the sand faces in well bores against the oil being driven to the wells by the existing low reservoir energy. When these conditions restrict oil production to uneconomic rates, the wells are abandoned and often plugged.

In this region the oil sands are too thin and occur at too great a depth to make redrilling of plugged fields a profitable enterprise. Consequently these fields must be kept in operation to conserve a great natural resource so important to this region and Nation. Most of these wells can be maintained and operated at a profit by repairing well-bore and surface equipment and by well clean-out work. Remedial work by many operators has proved that this can be done.

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During this fiscal year, engineers of the Franklin, Pa., office completed a comprehensive analysis of oil-well reconditioning practices and clean-out methods in use in the southern part of the Appalachian region. The report15/ appraises the efficiency of reconditioning methods used in the region through studies of records of 1,450 reconditioning jobs. Detailed data were obtained on 366 of the jobs, including pertinent information from well logs, descriptions of conditions of wells before clean-out, details of the clean-out work performed and its cost, and production statistics before and after the wells were cleaned.

Forty-eight graphs and tables are used in the presentation to illustrate the results obtained in well reconditioning and clean-out work by all methods in use.

A cost analysis, comparing the increase in oil-production rates obtained by cleaning and repairing old wells with rates of new production resulting from oil wells drilled in West Virginia during recent years, shows that an increase in the production rate of the area may be obtained as cheaply by reconditioning old wells as by drilling new ones. The report shows that the average reconditioned well produced 38.5 barrels of oil a month more than before rehabilitation at a cost of $23.25 for each unit barrel of increase in the monthly rate, whereas each barrel of oil per month produced from newly drilled wells is conservatively estimated to have cost $24.79.

Gravitational Drainage of Oil from Unconsolidated Sands

The large volumes of low-A.P.I. gravity oil that will remain in many shallow California fields when such oils no longer can be recovered profitably by pumping are important potential sources of oil when ways and means are found to recover some of the oil from the reservoir sands. As the quantities of oil that will be retained in the sands ultimately are so large and their recovery is such a challenge to petroleum engineers, the Bureau of Mines has studied the problem.

From time to time suggestions are made that a practical and economic method of recovering additional quantities of the retained oil from reservoir sands is to sink shafts to the sands and heat the oil remaining in the sands by installing steam lines in drifts or galleries radiating outward from the shafts.

To determine whether the application of heat in drifts or tunnels in partly depleted oil sands would result in the recovery of additional oil, a laboratory oil field was constructed, about 3 by 3 feet in area and about 1 foot thick, consisting of packed unconsolidated sand with 25 percent of the pore space filled with water and 75 percent with 13.1° A.P.I. oil from the Kern River field, Calif.

After 57 percent of the added oil and 28 percent of the added water had drained from the sand body through five wells, no more liquid drained from the sand while the temperature of the sand body was maintained at 84° F.

15/ Grant, Bruce F., Oil-Well Reconditioning in Southwestern Pennsylvania, West Virginia and Southeastern Ohio: Bureau of Mines Rept. of Investigations 4193, 1948, 82 pp.

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After an unsuccessful attempt was made to recover additional oil by means of an air drive, the wells were plugged, a tunnel was driven horizontally through the bottom of the sand body, and heating elements were installed by means of which the temperature in the tunnel was increased by 50° F. increments from 84° to 234° F. After heat was applied in the tunnel for 75 days, during which time the temperature was progressively increased from 84° to 234° F., only slightly more than 0.1 percent of the oil remaining in the sand after gravitational drainage to wells at a temperature of 84° F. was recovered.

When samples of sand were taken from the reservoir of the laboratory field for oil-saturation determinations at the end of the experiment, segments of cores from around the immediate vicinity of the tunnel were found to be caked. The appearance of the caked cores indicated that the heat had reduced the permeability of the sand about the tunnel and that caking of reservoir oil sands about drainage outlets is a factor to consider when warming oil sands by applying heat to the sand faces of tunnels or wells in partly depleted oil reservoirs.

A report describing the results of the experiment has been prepared for publication.16/

Recovery of Hydrocarbons from Bituminous Sandstones

During the past year work was completed on the laboratory study of a practical method for recovering hydrocarbons (bitumen) from bituminous sandstones of the outcropping Edna deposits near San Luis Obispo, Calif., and a report was prepared for publication.17/ The report describes the construction and operation of the laboratory separation plant and discusses the problems involved and the results obtained in treating Edna bituminous sandstones. The utilization of the recovered bitumen as a source of motor fuels, Diesel fuels, and fuel oils also is discussed and data on cracking, analytical distillation, and its asphalt properties are summarized.

The studies demonstrated that the hot-water method of separation may be applied satisfactorily to separating bitumen from the Edna sandstones. The process, as developed in the laboratory of the Petroleum Field Office at San Francisco, Calif., consists broadly of three operations:

1. Heating and mixing the bituminous sandstone with water and enough alkaline reagent to form an alkaline pulp in which the bitumen is displaced from the sand grains by the water. Efficient separation also depends on the occlusion of enough air in small bubbles in the pulp to form an oil froth.

2. Separating the oil froth from the sand by submerging the pulp in hot water. The oil froth floats to the surface of the water and the sand grains, freed of bitumen, sink to the bottom.

16/ Higgins, R. V., and Shea, G. B., Laboratory Studies of the Gravitational Drainage of Oil from Unconsolidated Sands: Bureau of Mines Rept. of Investigations 4391, 1948, 15 pp.

17/ Shea, G. B., and Higgins, R. V., Laboratory Study of the Hot-Water Process for Separating Hydrocarbons from Surface Deposits of Bituminous Sandstones near Edna, Calif.: Bureau of Mines Rept. of Investigations 4246, 1948, 31 pp.

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3. Removing the water, sand, and silt from the oil froth by dilution of the bitumen with a light oil and settling.

The presence of soluble mineral salts in the Edna sandstones consisting largely of iron and calcium sulfates with some sodium and aluminum sulfates made it necessary to water-wash the sandstones to remove these troublesome impurities.

Under optimum conditions of laboratory pilot-plant operation, including careful control of the pH of the treating system, about 25 gallons (95 percent) of the bitumen are recovered per ton of bituminous sandstone.

With discoveries of crude oil in California declining and known reserves being rapidly depleted, and the recovery of hydrocarbons from bituminous sandstones entirely feasible, their commercial recovery now is largely a matter of economics. The determination of the cost of recovering bitumen would require the building and operation of a pilot plant, which would involve mining, separation, and preliminary refining. Data from such operations would furnish the basis for sound estimates of the cost of recovery on a commercial scale.

Recovery of Wax from Crude-Petroleum Wastes

The economic handling and disposal of water-oil emulsions that accumulate in the bottoms of lease and refinery crude-oil storage tanks and in burning and storage pits are over-present problems of the petroleum industry. A large percentage of these emulsions are stable; and, since they cannot be resolved by ordinary field treating practices, they are unmarketable and represent a loss to the producer and refiner. A method of recovering oil from such emulsions was developed by Bureau of Mines technicians at Bartlesville, Okla., and was perfected in a field pilot plant near El Dorado, Kans. The results of this study are presented in a report[18] completed during the year.

Three variations of the method developed are described in the publication. These have been classed as (1) the batch quiescent settling method, (2) the semicontinuous-flow method, and (3) the continuous method. The batch method, which was used exclusively on residual pit-waste emulsions, consists of four steps: Procuring the emulsion, liquefying and screening it, treating, and allowing to settle. The semicontinuous-flow method is a modification of the batch method and was used successfully in treating tank-bottom settlings. The continuous method substitutes mechanical agitation, thermal dehydration, and filtration instead of settling. Although the continuous method requires further study, results obtained by its use indicate that it may have application for resolving tank-bottom settlings.

A total of 2,000 barrels of pit-waste emulsion was treated in the pilot plant; 600 barrels of clean oil were recovered. The emulsion contained an average of 57 percent water, 3 percent sediment, and 3,500 pounds of sodium chloride per 1,000 barrels of emulsion, while the recovered clean oil averaged

18/ Horne, Joseph W., and Watkins, J. Wade, A Method of Resolving Oil-Field Waste Emulsions: Bureau of Mines Tech. Paper 715 (in press).

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0.6 percent sediment, no water, and 12 pounds of sodium chloride per 1,000 barrels of oil. The recovered oil contained 15 to 18 percent microcrystalline wax with a melting point between 165° and 170° F., and was also suitable for refinery cracking stock.

Laboratory Studies

Electrical Analogy Flow Studies of Gas-Injection Projects

An electrolytic model apparatus utilizing the similarity between Ohm's law of electrical circuits and d'Arcy's law of flow through porous mediums has been employed in the laboratory of the Franklin, Pa., office on engineering field studies of gas-injection projects. Although the flow of ions through the electrolyte utilized in the model is not strictly comparable to the flow of gas, oil, and water through sandstone reservoirs the data derived are quite useful in reservoir engineering studies. In fact, some data obtainable with the model can be derived in no other way except partly by developing an oil field and depleting it of its hydrocarbon content. Obviously the advantage of the model is that needed information can be derived before the field development is undertaken.

In the Appalachian region, particularly where the oil sands are thin and occur comparatively deep (thus excluding the probability of redevelopment of old fields for secondary recovery operations), the model is useful in determining which existing wells among those drilled in an irregular pattern and spacing may be used to best advantage as injection wells to drive the greatest quantity of oil to the producing wells with the expenditure of the least amount of energy. Thus a choice of use of wells most likely to lend themselves to the most efficient operation of the field can be made before development capital is spent. The model is useful in studies of both waterflooding and gas-injection problems.

For example, the study of one gas-injection project in West Virginia, in operation for 20 years, disclosed the probability that, by using additional injection wells, the operator could have produced at least 25 percent more oil in the same time without utilizing additional energy or capital. This increase in oil recovery would have been realized despite the utilization of some of the oil wells as injection wells, for the study considered only the wells in use during the gas-injection operations.

Laboratory at Franklin, Pa.

A laboratory is maintained at the Franklin, Pa., office to test and study oil-formation specimens (cores) for: (1) Porosity; (2) permeability; (3) oil and water saturation, and their physical and chemical characteristics; (4) sand grain size and distribution, by sieve analysis; (5) sand pore size and shape by microscopy; and (6) connate water saturation by restored-state capillary pressure. Other experiments correlate residual oil saturations after laboratory air-drive with pore pattern of sandstones. Apparatus is available for testing oil-base and water-base drilling fluids. Facilities are available for making mineral analyses of waters, including oil-field brines. A laboratory apparatus for determining the fundamental characteristics of vertical flow of gas and liquid through small-diameter pipes is in use to provide design data for siphon-flowing oil production on gas-injection projects.

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Oil-formation specimens procured in the Appalachian region from wells drilled on secondary-recovery projects, and others obtained in connection with special scientific investigations of reservoir characteristics being studied by Bureau engineers, are analyzed. During the year six cores were analyzed in connection with the oil-base mud cable-tool coring studies described elsewhere in this report. An improved permeameter was designed and built. The new cabinet-housed apparatus expedites permeability measurements of sandstone specimens.

Connate-water determinations by the capillary pressure or restored state method were made on six specimens of oil-producing sandstone. Glass apparatus utilizing fritted-glass-supported semipermeable membranes of barium sulfate were used. The brine in the previously saturated core specimens was displaced with kerosine during tests by imposing air pressure at not to exceed 15 psi on the surface of the kerosine. The physical strength of the glass apparatus was not great enough to allow pressures high enough to reach an irreducible brine saturation when some sandstone specimens were tested. A stronger, improved apparatus must be acquired before tests can be made a part of routine core analysis.

Laboratory experiments on air-drive expulsion of oil and water from "fresh" and laboratory-saturated rotary cores are being conducted. The work is done with so-called flood pots, which are operated in a manner to simulate air-drive secondary-recovery operations in the field. Each test is terminated when the produced-air : oil ratio reaches values comparable to limiting economic operations in practice. One objective is to learn if there is a relationship between the volume of oil recovered from the core in the flood-pot test and the grain-size distribution, determined by sieve analyses on adjacent pieces of the same core, taking into account the viscosity of the fluids used and the rock characteristics determined by routine core analyses on the same pieces of core used in the sieve tests. Several different rotary-sand cores and crude oils are used in these investigations. Microscopy of pore pattern on adjacent pieces of the same rotary core is being carried on simultaneously in an effort to fit this important characteristic of sandstones into the relationship.

Laboratory at Bartlesville, Okla.

The core and water laboratory at Bartlesville, Okla., provides essential factual data for studies of secondary-recovery methods and practices. During the past year 136 routine water analyses were made. Since its inception in 1923, the laboratory has analyzed nearly 2,000 water samples, and the results of these determinations are available to all for study and comparison. The porosity, permeability, and oil saturation of 197 oil-well core samples were determined during the past year. About 2,500 core samples have now been analyzed by the laboratory, and the results are on file at the station. To determine the possibility of water-injection wells being plugged by the reaction of mixed waters, special water analyses were made to determine the barium, strontium, iron, and sulfate content of several samples.

The installation and operation of equipment to determine connate water content of cores by the restored state method were important additions to the

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work of the core and water laboratory during the past year (see fig. 7). This equipment and procedure differ somewhat from those used at Franklin; although the original equipment was not designed by Bureau engineers, certain changes and improvements in equipment and technique of operation at Bartlesville were necessary to obtain usable results. Since September 1947, 146 core samples from wells in 4 fields have been tested for minimum water content. It was found that surface tension of the saturating brine was an important characteristic that influenced the residual water saturation of the core at normal displacing pressures. For this reason, wherever possible, the natural brine was used to saturate cores. Where this was not practical, a prepared brine with a comparable surface tension and mineral content was used. For future reference and determinations of surface and interfacial tensions, a library of brine samples has been established in the laboratory.

Surface tension, interfacial tension with distilled water, specific-gravity, and viscosity measurements were made on 17 crude-oil samples from the Martha field, Johnson and Lawrence Counties, Ky. The surface and interfacial tensions were determined at 90° F., so that results could be correlated with those obtained in 1934 on samples from the same wells and published in Report of Investigations 3325 entitled, "A Study of Oxidation of the Oil in Two Air- and Air-Gas Repressuring Projects."

Fundamental Research

Nature of Surface Forces Retaining Oil in Sands

Behind each published report is much careful and painstaking work in the laboratory and in the field to provide the tools, methods, and data of research. Some of this work is fundamental in nature, with widespread applications to many problems but peculiar to none. Such a program is the study of those forces that tightly bind petroleum to the reservoir rock and prevent extraction of a large portion of the crude oil originally present. At the Petroleum Experiment Station, Bartlesville, Okla., a laboratory is being equipped and personnel recruited to initiate studies which, it is hoped, may ultimately aid in decreasing the residual-oil saturation of sands in depleted oil fields. The general problem is being attacked from several angles, which include a study of the identity and properties of the film-forming substances in petroleum, studies of the attractive forces between the liquid and solid phases in petroleum reservoirs, studies of the forces governing the movement of fluids through porous mediums, and studies of the interfacial tensions in crude oil-water systems.

PETROLEUM CHEMISTRY AND REFINING

The availability of fuels for all types of internal-combustion engines remains the keynote of research in petroleum chemistry and refining, as it has been during the last several years and as it is projected into the future for some years to come. Availability - in the sense used here - embraces a very broad significance. It relates not only to actual at-hand production of petroleum products but also to the relationships the properties of these products and their composition may have to supply, as well as effects of technical changes in utilization and consumer demands. The term "fuels" includes both motor and aviation gasolines, Diesel fuels, and gas turbo fuels

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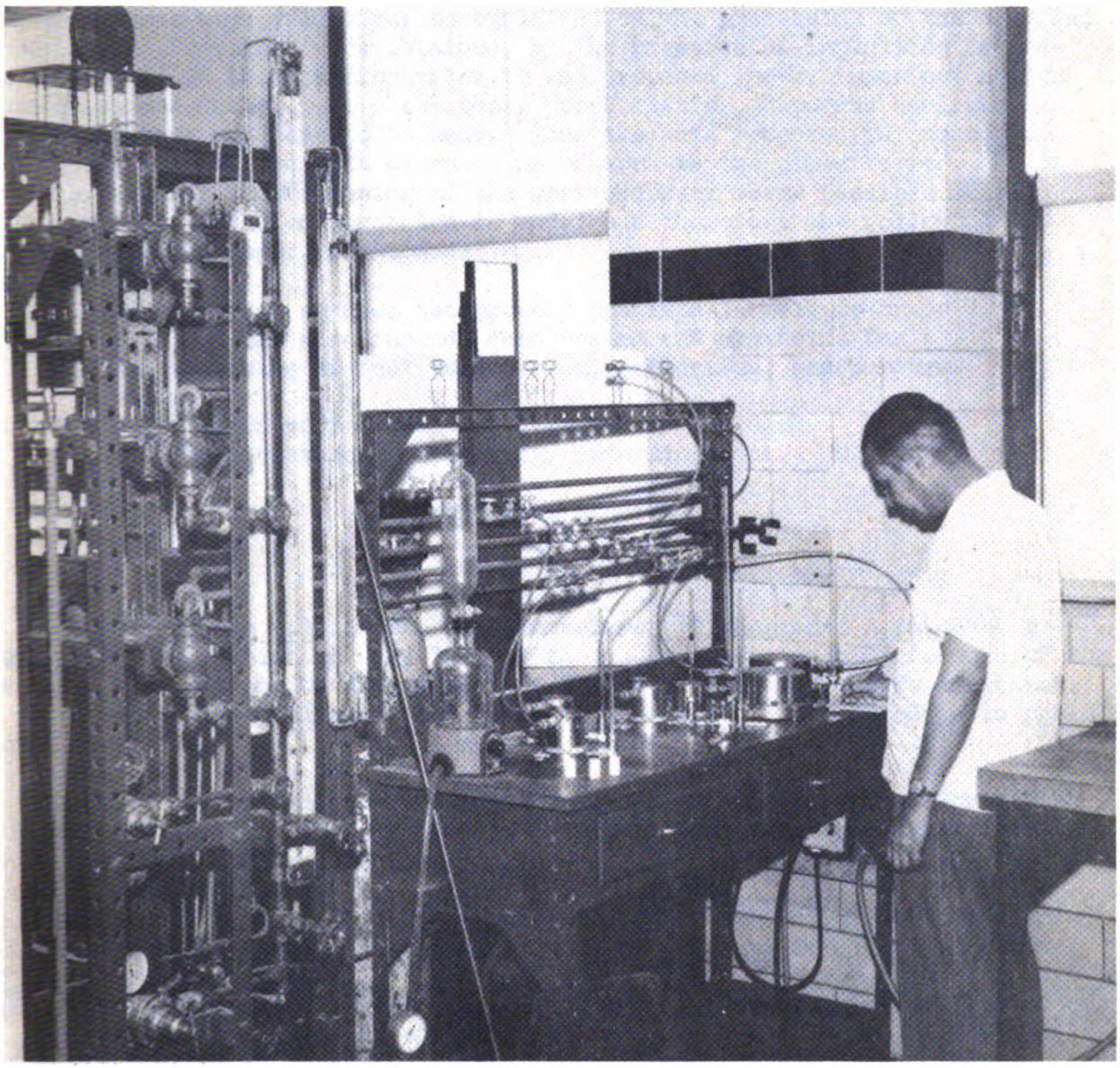

Figure 7. - Determining connate-water saturation by restored-state method.

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and covers petroleum products having a boiling-point range from about 100° F. to about 750° F. This scope includes approximately 50 percent of most crude oils. This is indeed a wide and fertile field for research.

Following the pattern established in the 1947 report,[19] the material to be discussed is divided into four categories. Although these topics will be discussed independently, they are nevertheless closely related. For example, if fractions prepared from a crude oil are found to have unusually high cetane numbers, these high values may be explained by the processing of the material by which the fractions were obtained, by the presence of impurities or compounds formed in the fraction after it was prepared, or by imperfect estimation of cetane number. To check these possibilities, numerous analyses by various methods may have to be made. Thus the data reported in one topic are intimately related with discussions of work in the other topics. Nevertheless, clearer understanding of the work underway seems possible if a division such as the one proposed is made, and therefore the following discussion is given under four topics:

1. Raw-material studies (at present confined largely to crude oil, but may also include condensates and synthetic fuels).
2. Relationships of fuel composition, properties, and performance.
3. Utilization of petroleum products.
4. Analytical methods and property determinations.

Raw Material Studies

Crude Oils

Domestic Crude Oils. - The 1947 annual report mentioned a paper[20] prepared for presentation in July 1947 at the Chemical Research Conference of the American Association for Advancement of Science. From the topics discussed in that paper, two publications have already emerged, and a third is in preparation.

One publication was an imaginative map called "The Petroleum World." This was illustrated and described in detail in the 1947 report and published in Chemical and Engineering News.[21]

The second paper resulted from discussions of the sulfur content of crude oils and in final form[22] was presented at the American Petroleum Institute

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19/ Cattell, R. A. and others, Report of Petroleum and Natural-Gas Division, Fiscal Year 1947: Bureau of Mines Inf. Cir. 7484, 1948, pp. 31-51.

20/ Smith, H. M., Composition of American Petroleum: Pres. at Chemical Research Conference, Am. Assoc. Adv. Science, June 30 - July 4, 1947, New London, N. H.

21/ Smith, H. M., The Petroleum World: Chem. Eng. News, vol. 26, Apr. 19, 1948, p. 1150.

22/ Smith, H. M., and Blade, O. C., High-Sulfur Crude Oils of the United States - Trends in Supply: Proc. Am. Petrol. Inst., vol. 27, sec. 3, 1947, pp. 119-141. Also, in slightly different forms, in Oil and Gas Jour., Nov. 29, 1947, pp. 73-78; Petrol. Refiner, May 1948, pp. 101-110.

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meeting in Chicago in November 1947 and reprinted in two trade journals. According to this paper, the total production of high-sulfur crude oils reached a new high in 1946, although the ratio of high-sulfur crude oils produced to low-sulfur crude oils remained the same as for the preceding year. However, the relative sulfur contents of the estimated reserves of the country show approximately the same pattern in distribution as do the sulfur contents of crude oils currently produced, which would indicate that, until new fields of considerable magnitude are discovered, the ratio of high-sulfur to low-sulfur crude oils should not change materially. Most of the major petroleum districts of the country are now producing greater volumes of high-sulfur crude oils than at any previous time in their histories; and in most instances this is true, whether in terms of millions of barrels produced or as percentage of the Nation's total oil. A great deal of the oil having a high sulfur content is in the range above 1 percent sulfur, and even a good portion of that has more than 2 percent sulfur.

These conclusions are drawn from consideration of data in the paper covering 1915-46. Table 2 summarizes the information given and the distribution of sulfur content for total crude-oil production in the United States for 1915-46 is shown in figure 8.

TABLE 2. - Summary of United States crude-oil production between 1915 and 1946 on the basis of the sulfur content of the crude oil

Year	High-sulfur (over 0.5 percent sulfur)		Low-sulfur (0 to 0.5 percent sulfur)		Ratio of high-sulfur to low-sulfur
	(Millions of Barrels)	(Percent)	(Millions of Barrels)	(Percent)	
1915...	95	34	186	66	0.51
1920...	144	33	299	67	.48
1925...	339	44	425	56	.80
1930...	382	43	516	57	.74
1935...	295	30	702	70	.42
1940...	444	33	909	67	.49
1946...	608	35	1,125	65	.54

Although the Bureau of Mines has published many reports of crude oil analyses for individual areas within the country, only two reports of crude oil analyses on a nation-wide basis have been issued. One is Bulletin 291,[23] published in 1928, and the other is Report of Investigations 4289,[24] published in May 1948. This new report presents analyses of crude oils from 283 important fields in the United States, each of which has a production of 2,500 barrels a day or more. The compilation therefore represents a very large percentage of the entire crude-oil production of the country. This particular paper undoubtedly will be used extensively by oil producers, geologists, buyers, refiners, research workers, and others working on petroleum chemistry relating to crude oils.

23/ Smith, N.A.C., and Lane, E. C., Tabulated Analyses of Representative Crude Petroleum of the United States: Bureau of Mines Bull. 291, 1928, 69 pp.

24/ McKinney, C. M., and Blade, O. C., Analyses of Crude Oil from 283 Important Oil Fields in the United States: Bureau of Mines Rept. of Investigations 4289, 1948, 154 pp.

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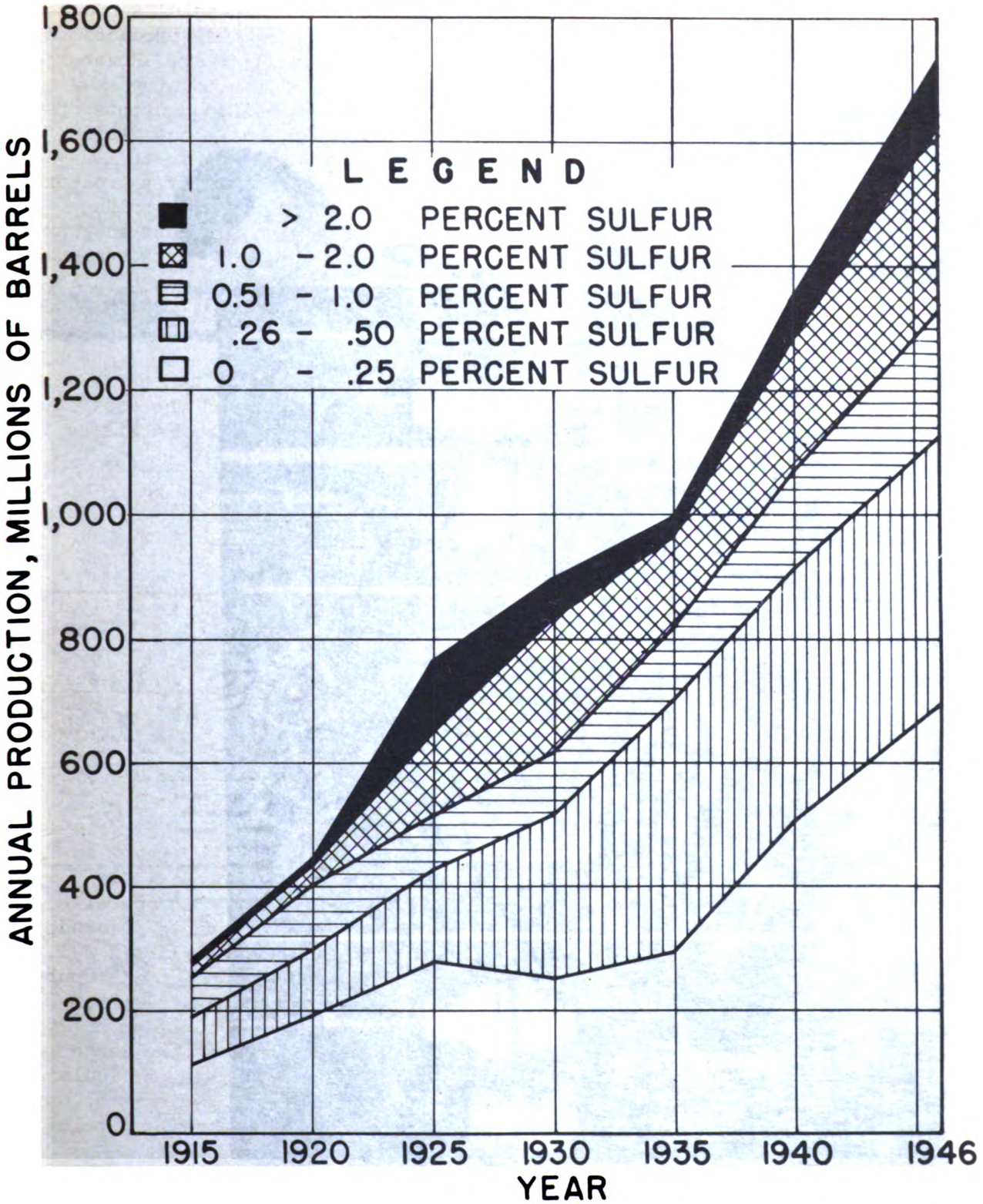

Figure 8. - Relationship of crude-oil production and sulfur content of crude oil for 5-year periods, 1915-46.

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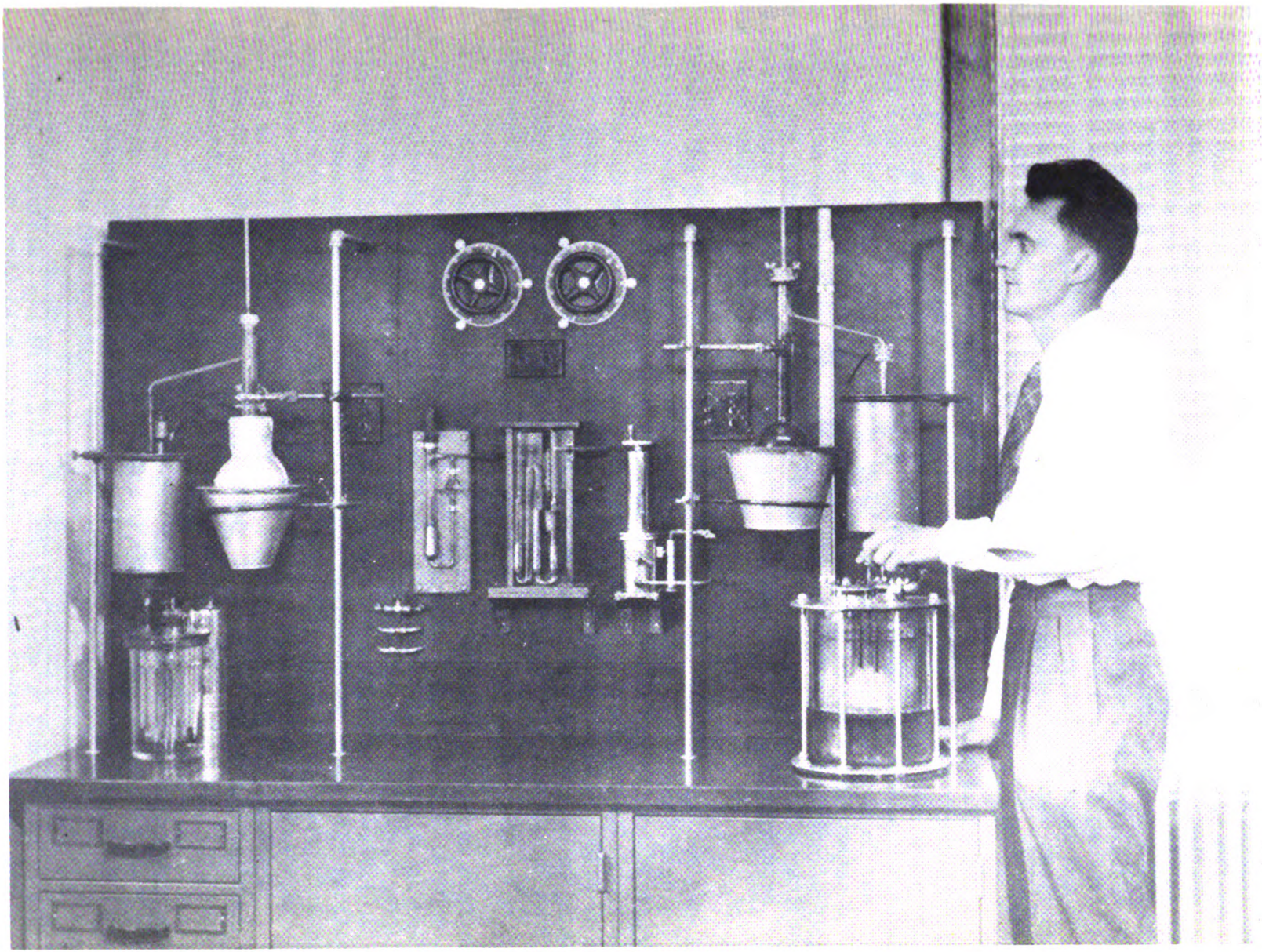

Figure 9. - Crude-oil-analysis apparatus.

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For over a quarter of a century, the Bureau of Mines has sought to make public information regarding crude oils and their characteristics and in so doing has analyzed many samples of petroleum by its standardized routine method. Most of these analyses have been published, sometimes in special compilations, other times in connection with reports of research in petroleum. As is the case with any accumulation of data, finding individual analyses becomes more and more difficult as the accumulation increases. To assist in overcoming this hindrance, a finding list of individual analyses or bibliography of reports containing analyses of crude oils has been prepared and issued as an information circular.25/ The report consists of two essential parts: (1) A bibliography of 115 references to publications containing analyses of crude oils; and (2) a finding list of 2,457 crude-oil samples whose analyses have been published.

The 1947 annual report referred to a bulletin tentatively entitled "Routine Crude-Oil Analyses," to consist of several parts. The first part of this, describing the Bureau of Mines routine analytical method for crude oils, is almost completed and will be submitted for publication in the near future. Parts 2 and 3 of this bulletin, which deal with the interpretation of the analytical data, are advancing rapidly and should be in the final stages by the end of the coming year. The interpretation of crude oil-analyses is very exacting, and considerable study is necessary to present clearly the various interpretations that can be made and can be applied to petroleum products from these analytical data.

During the past year at the Bartlesville Station, 101 routine analyses of domestic crude oils were made. The majority of these were from Texas, California, and Kentucky; however, Oklahoma, Illinois, Arkansas, and Montana each had four or more. Efforts are continuing to keep the crude oil analysis file up-to-date. Fifty-six samples are on hand awaiting analysis, which is an improvement over last year at the same time, when 86 samples were on hand. Approximately 40 additional samples from fields not previously analyzed have been requested.

At the Laramie Station, a method was developed whereby crude-oil analyses may be made by the Bureau of Mines method in laboratories at high altitudes to give results directly comparable to those obtained in laboratories at sea level. Modification of the usual equipment has been made so that the initial distillation may be carried out under a pressure equivalent to sea-level pressure. Numerous tests of this pressurized equipment on crude oils indicate that results are obtained which check within experimental error those obtained at sea-level laboratories. The method becomes necessary when laboratories operate at altitudes higher than 2,000 feet. Many such laboratories are located in the Rocky Mountain region. Figure 9 pictures the apparatus used in this method.

Continuing the program of obtaining crude-oil analyses on representative Rocky Mountain crude oils, at the Laramie Station 11 analyses were made during the year. Eight of these were on crude oils from Colorado fields, while three were on crude oils from Wyoming.

25/ Hughes, Elizabeth, and Blade, O. C., Bibliography of Reports Containing Analyses of Crude Oils by the Bureau of Mines Routine Method: Bureau of Mines Inf. Circ. 7470, 1948, 68 pp.

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Foreign Crude Oils. - The Bureau of Mines is attempting to procure and analyze samples of crude oils from foreign fields. During the past year 27 samples of foreign crude oils were analyzed, of which 19 were from South America and 8 from the Middle East and vicinity.

In addition to the usual routine analyses which will be made on all of these samples, most of the samples have been obtained in 5- or 50-gallon quantities, which permit analyses of a more extended nature, similar to those made by the Bureau during World War II in evaluating aviation-gasoline base stock contents of various crude oils. Base-stock studies of the South American oils are being made in the same manner. A sample of the crude oil is distilled and the cuts are made at 100°, 200°, 242°, 285°, and 320° F. The maximum number of cuts, excluding cut 1, which will yield 91-octane-number aviation-gasoline base stock, are then blended and properties determined. For some samples superfractionation is being applied and the "iso" cuts, and "normal" cuts from isohexane through isodecane are being prepared. The high-octane-number iso cuts are then blended and rated for their suitability as blending agents for high-octane-number aviation gasoline. During the past year 10 crude oils have been evaluated according to one or the other of these two methods.

Relationships of Fuel Composition, Properties, and Performance

Gasoline

Superfractionation studies of naphthas continue to interest the petroleum industry, and the Bureau of Mines has continued its work in this field during the current year by a superfractionation of the naphtha from a West Edmond, Okla., crude oil. This study differed from previous studies in that the naphtha was prepared from the crude oil by processing in a pilot-scale continuous still built by Bureau personnel. A 100-gallon sample of the naphtha was superfractionated into 0.5-percent fractions in the 100°-300° F. boiling range. Each fraction was analyzed for composition in terms of individual hydrocarbons and its octane number by the Motor Method (ASTM D357) determined. In figure 10, the overhead distillation temperature and octane number are plotted against the percentage distilled. The composition and combustion data will be used to improve the accuracy of the Motor Method, blending octane numbers of the individual hydrocarbons that were calculated from data obtained on Oklahoma City[26] and Santa Barbara,[27] Venezuela, naphthas.

Diesel Fuel

A problem of primary concern to almost every organization dealing with petroleum is the unprecedented demand for oils in the Diesel-fuel boiling range. This boiling range includes not only Diesel fuel but also domestic fuel oil, jet-propulsion fuel, and charging stock for catalytic cracking units

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26/ Ward, C. C., Gooding, R. M., and Eccleston, B. H., Superfractionation Studies; Composition and Octane Number of 0.5% Fractions of an Oklahoma City Naphtha: Ind. Eng. Chem., vol. 39, January 1947, pp. 105-109.

27/ Schwartz, F. G., Gooding, R. M., and Eccleston, B. H., Superfractionation Studies: Naphtha from Santa Barbara, Venezuela, Crude Oil: Ind. Eng. Chem., vol. 40, November 1949, pp. 2166-2169.

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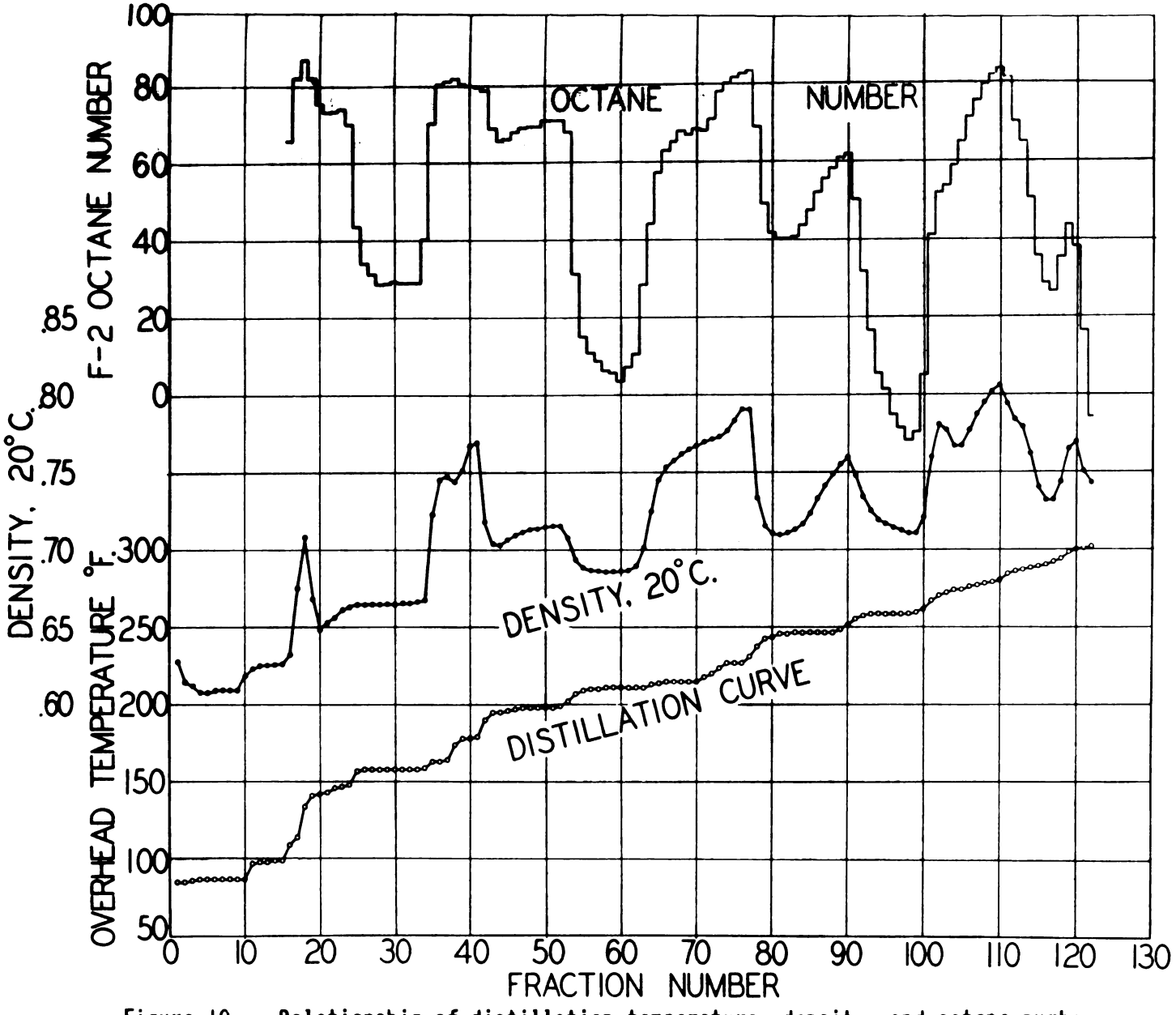

Figure 10. - Relationship of distillation temperature, density, and octane number of naphtha fractions from West Edmond, Okla., crude oil.

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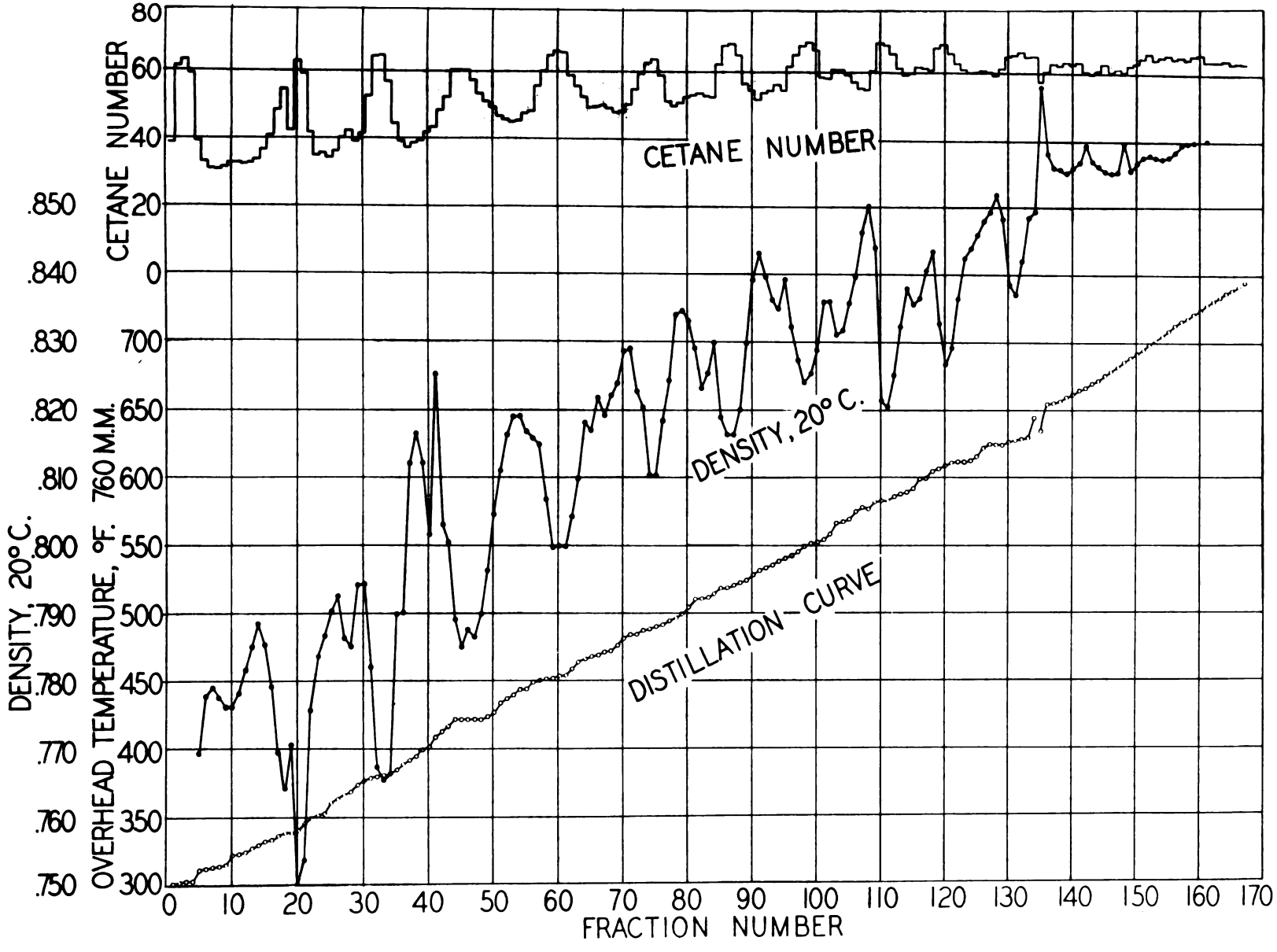

Figure 11. - Relationship of distillation temperature, density, and cetane number for Diesel-fuel fractions from West Edmond, Okla., crude oil.

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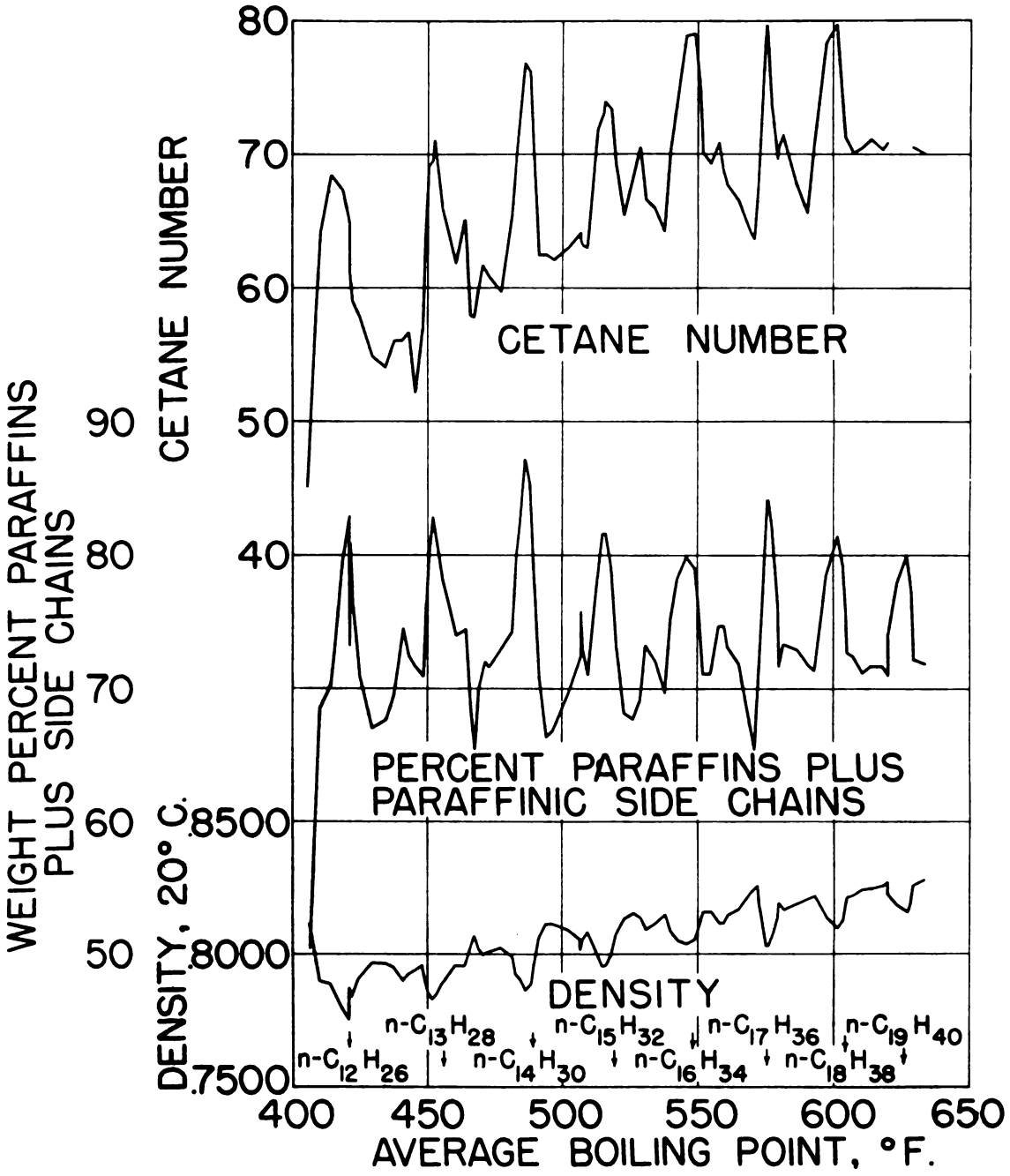

Figure 12. - Relationship of density, percentage of paraffins plus paraffin side chains, cetane number, and boiling point for paraffin-naphthene fractions of West Edmond, Okla., Diesel fuel.

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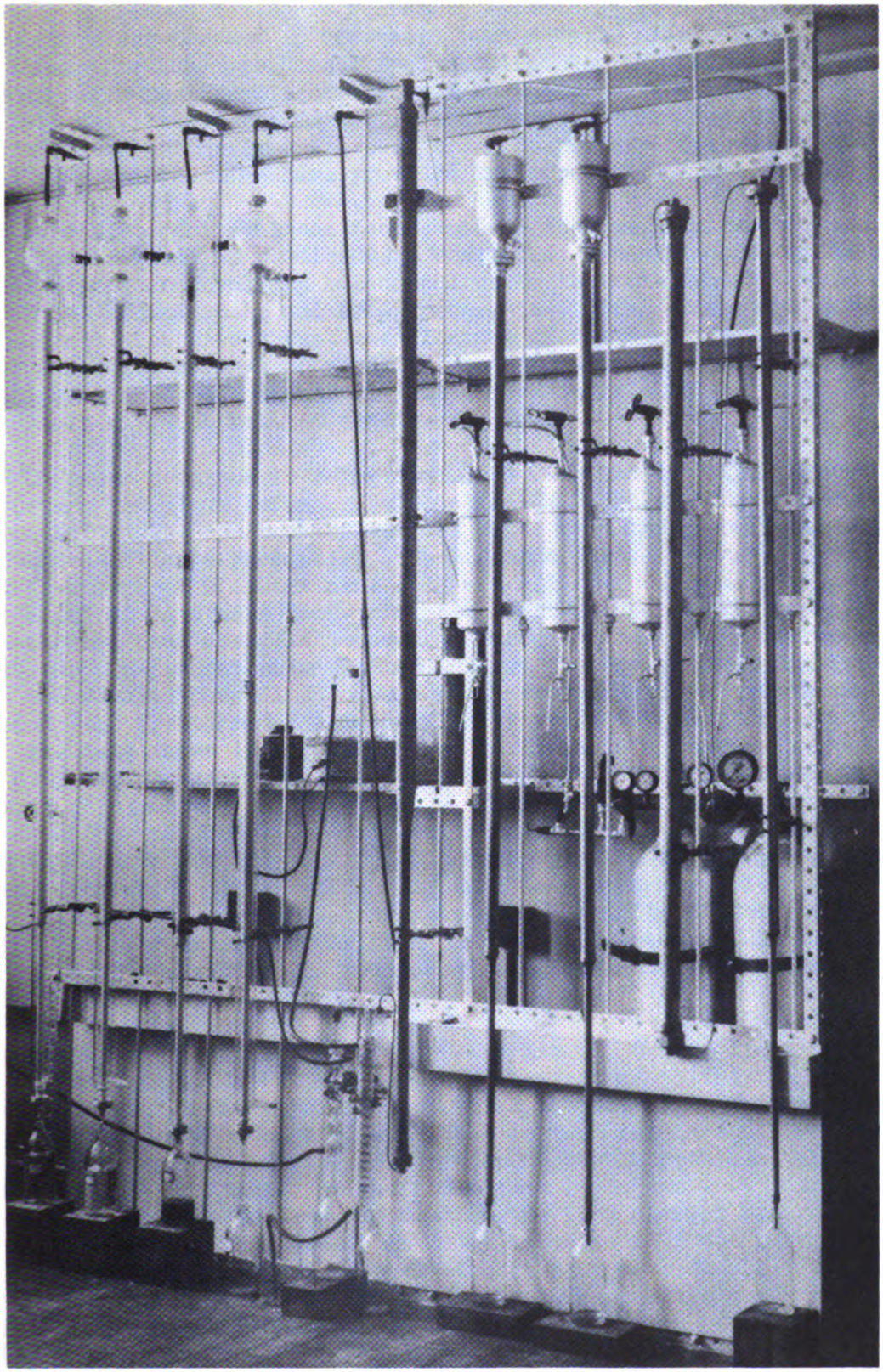

Figure 13. - Silica-gel columns used to separate paraffin-naphthene and aromatic fractions from Diesel fuels.

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making gasoline. It is anticipated that the supply will become more critical as a greatly increased demand is forecast, especially in Diesel fuel for railroad locomotive service and in household burner fuel. Furthermore, the specifications for the type Diesel fuel required for the modern high-speed Diesel engine are much more restrictive than those for the older, low-speed units. This makes knowledge of the relationships between fuel composition and ignition characteristics imperative in order to prepare improved fuels. Both motor and aviation gasoline have provided analogous situations in past years.

The Bureau recognized these facts, and as soon as commitments relating to wartime aviation-gasoline studies were completed, Bureau technologists started an intensive program involving basic studies on the relationships between the composition of Diesel fuels and other properties. Other technical organizations concerned with Diesel fuel soon learned of the Bureau's program in this field; as a result, several cooperative programs have been initiated with these organizations whereby the Bureau will supply basic data on the composition of the same fuels on which related studies are made.

One of these programs is being conducted with the technical cooperation of the Western Petroleum Refiners Association (W.P.R.A.); it involves preparation of Diesel fuels from each of several crude oils that were selected as representative of large production. West Edmond, Okla., crude oil was selected as a typical Mid-Continent oil, and all of the processing and most of the analytical data have been completed on the 300°-740° F. cut. Figure 11 shows the overhead distillation temperature, the density, and the cetane number of the 0.5-percent cuts plotted against percentage distilled. A low value in the density curve indicates a high concentration of paraffins; and, as expected, the fractions having a low density value have a high cetane number. The data shown in figure 11 were included in a progress report presented to the Diesel Fuel Committee of the Western Petroleum Refiners Association at a meeting in August 1947. Figure 12 is from a report[28] presented before the Society of Automotive Engineers in Detroit in January 1948 and shows data for the paraffin-naphthene portion of three West Edmond fractions, from which the aromatic compounds have been removed by silica-gel filtrations. The curves illustrate that the density minima coincide with maxima for both percentage of paraffin plus paraffin side chains and cetane number; in turn, the minima and maxima coincide with the boiling point of the normal paraffins.

Separation of the fractions of the West Edmond, Okla., distillation with silica gel was concluded. As the samples became progressively higher in boiling point, changes in the physical properties of the sample necessitated changes in procedure and techniques. These in turn required alterations in column design to provide adequate separation of the hydrocarbon types. For the higher-boiling fractions, it was found that a pentane wash after the main paraffin-naphthene portion was removed provided sharper separation from the aromatic portion. This was followed by desorption of the aromatics with benzene, followed in turn by isopropyl alcohol to remove the residual tarry and resinous components. The columns used in this work are shown in the accompanying photograph (fig. 13).

28/ Smith, H. M., Preliminary Report of Studies on the Composition and Physical Properties of Diesel Fuels: Soc. Auto. Eng. Quart. Trans., vol. 3, No. 1, January 1949, pp. 164-177.

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The Bureau is analyzing three selected Diesel fuels for the Navy as a part of that agency's extensive program on Diesel fuels as related to future sources of supply. The three fuels that were selected are a Fischer-Tropsch fuel, a catalytically cracked fuel, and a Navy-specification fuel.

Preliminary tests on the Fischer-Tropsch fuel as received indicated that it contained 2 or 3 percent of oxygenated compounds. To simplify the analytical studies, these compounds were removed by percolating 80 gallons of the fuel through silica gel. About 75 gallons of the treated fuel were charged to the superfractionator used in previous studies. One hundred seventy-seven fractions were collected; and the density, refractive index, and bromine number of each were measured. A portion of each sample was sent to the Naval Engineering Experiment Station for cetane-number determinations. Figure 14 shows the overhead temperature and the cetane-number values that are currently available, plotted against the percentage distilled. This fuel was known to be composed largely of normal paraffins and the well-defined plateaus corresponding to the boiling points given in the literature for the normal paraffins bear this out. This fuel had a cetane number of 84 as received and after percolation through silica gel it was 88, so very high values for some of the fractions were anticipated. As shown on the curve, several fractions have a cetane number of more than 100. This presents a problem, as the standardized method for determining the cetane number makes no provision for values over 100. The Bureau has suggested to the Coordinating Research Council and the American Society for Testing Materials that a standard procedure be established to rate fuels having cetane numbers over 100, and the A.S.T.M. has organized a committee to work on this problem.

The 29-cetane-number catalytically cracked Diesel fuel is much more complex than the Fischer-Tropsch fuel, as it contains naphthenes and aromatics in addition to paraffins and olefins. One hundred gallons of this fuel was fractionated into 0.5-percent fractions; and the density, refractive index, and bromine number were measured for each fraction and a portion of each sample sent to the Naval Engineering Experiment Station for cetane-number determination. It is planned to percolate another portion of each fraction through silica gel to separate it into a paraffin-naphthene and an aromatic portion. Physical and chemical properties, including cetane number, will be determined on both portions. This new program of silica-gel separations involves fractions containing a larger percentage of aromatics than those studied in the West Edmond investigation; and, based on experience from that study, a stainless-steel column has been designed to accomplish this work more efficiently. A battery of six such columns has been constructed and erected and are at present in the testing stage.

A third cooperative Diesel-fuel program in which the Bureau is participating is sponsored by the Society of Automotive Engineers. The Bureau's role in this program is to obtain fundamental data on the composition of a straight-run Diesel fuel and on a catalytically cracked Diesel fuel which the Caterpillar Tractor Co. and the University of Wisconsin are studying intensively as regards combustion phenomena. In the Bureau's study, these fuels were percolated through silica gel and divided into paraffin-naphthene and aromatic portions before fractionation, as contrasted to the treatment of West Edmond Diesel fuel where the silica-gel treatment of the fractions followed the

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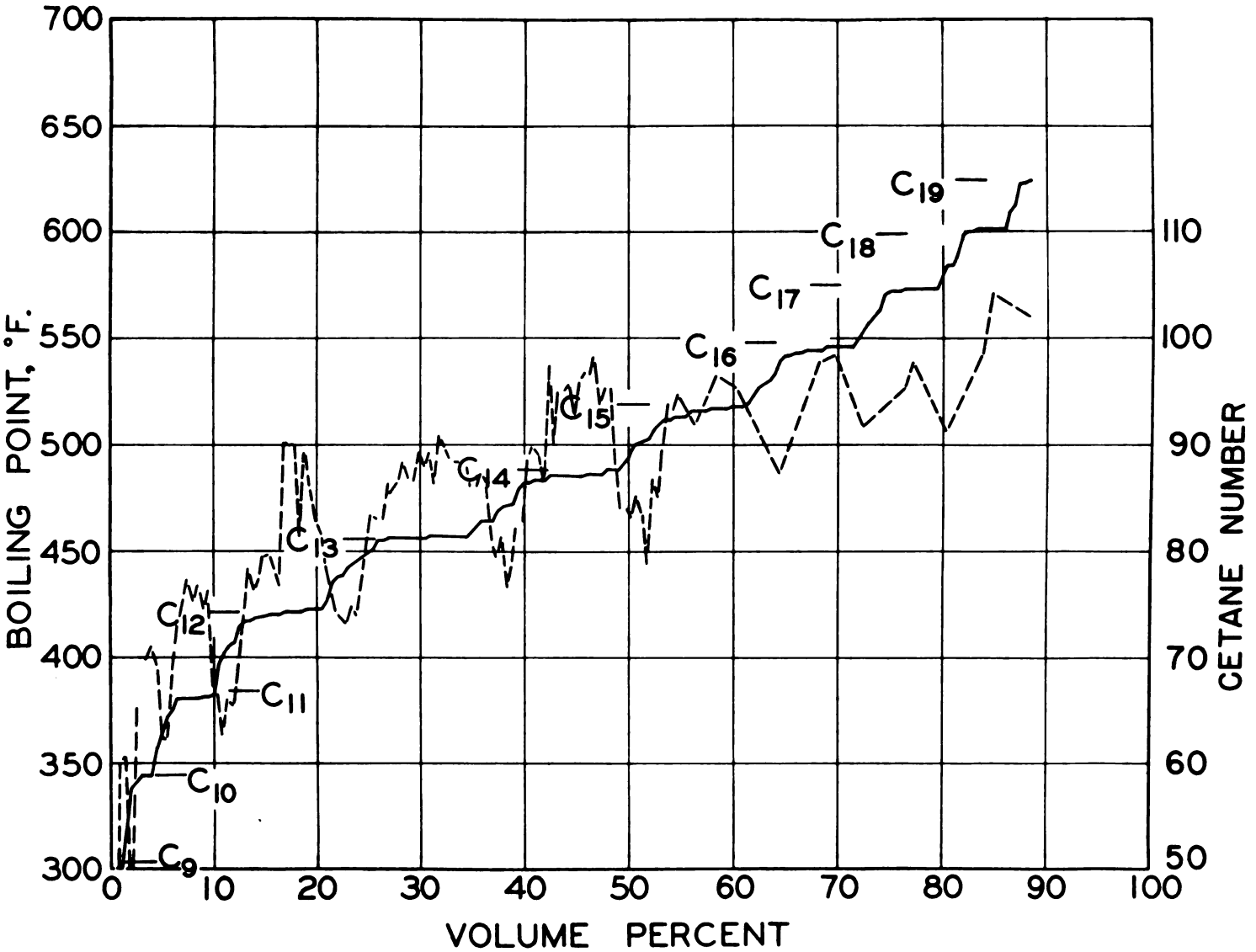

Figure 14. - Relationship of boiling point, cetane number, and volume percent of vacuum-distillation fractions of a Fischer-Tropsch Diesel fuel.

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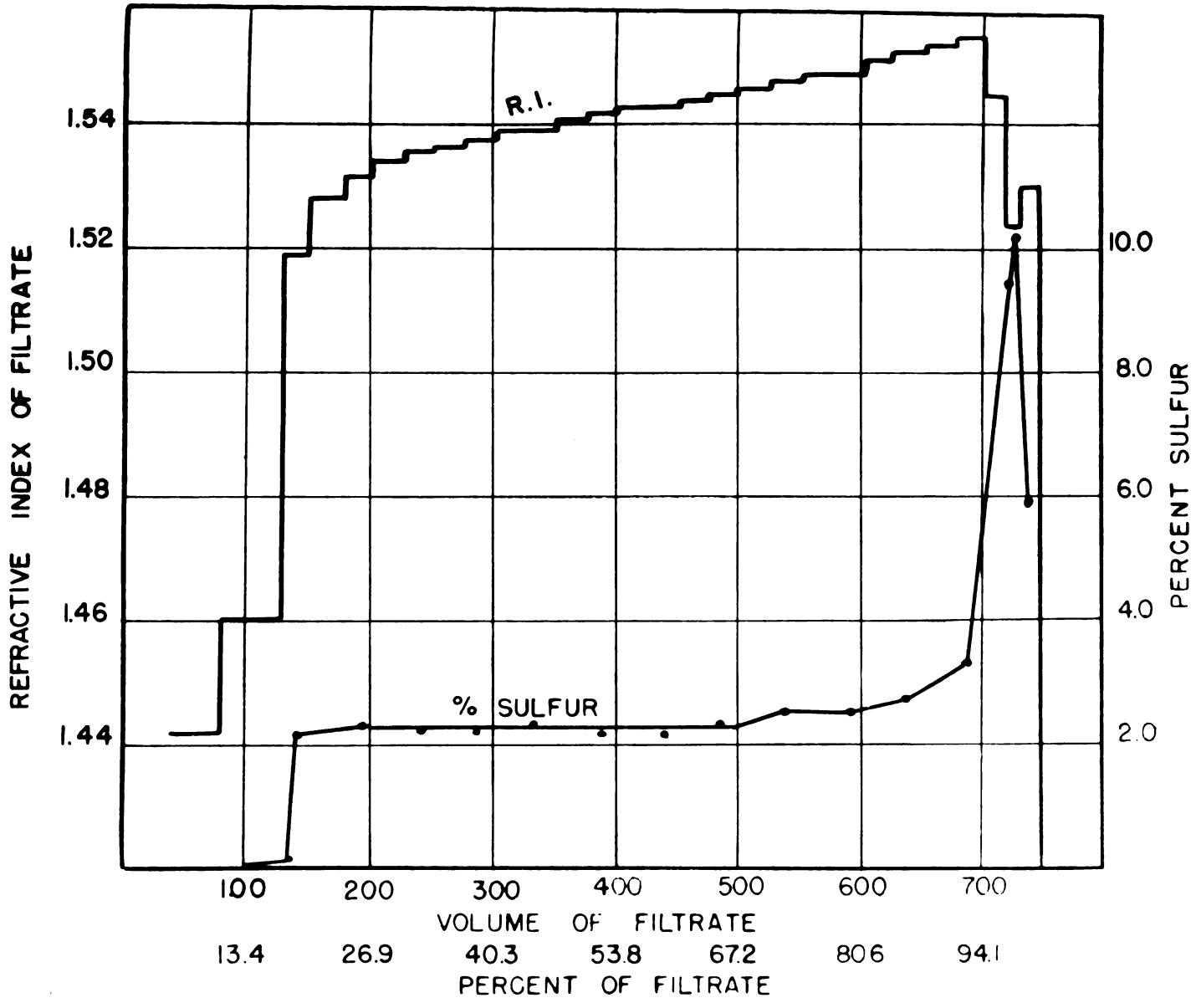

Figure 15. - Distribution of sulfur in fractions from a high-sulfur Diesel fuel, as obtained by filtration through silica gel.

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fractionation. The results of studies on these two fuels were presented at the Annual Meeting of the Society of Automotive Engineers[29] and later before the Mid-Continent section of the same society.

The data and conclusions from this paper are too extensive to reproduce here, but in general, the preliminary work showed that the straight-run Diesel fuel contained about 80 percent of paraffins and naphthenes, where a cracked stock had only about 61 percent; that the ratios of paraffins to naphthenes are somewhat higher in cracked stock; that normal paraffins are important components of both oils; that there are indications of the presence of dicyclic naphthenes; that there is fairly definite evidence of the presence of dicyclic and tricyclic aromatics, such as naphthalene, methyl and dimethyl naphthalenes, anthracene, and possibly diphenyls; that the aromatics in cracked stock have a much high proportion of di- and tri-cyclic compounds than are found in the straight-run material; and that olefins seem to play only a minor role in both oils.

The Bureau is also cooperating with Subcommittee XXV of Committee D-2 of the American Society for Testing Materials in developing a method for analyzing Diesel fuels to show the principal types of hydrocarbons present. A member of the chemistry and refining staff is head of the group working on this problem, and the studies the Bureau has made have contributed considerably to the success of this project.

Since 1945 the Bureau of Mines has been using silica gel to separate samples into a paraffin-naphthene raffinate and an aromatic extract. During these studies, it was noted that any sulfur compounds present in the sample remained in the aromatic portion. It appeared that silica-gel treatment might be a satisfactory analytical tool for concentrating the sulfur compounds in a small fraction of the original sample if a procedure was developed that was selective for sulfur compounds. An opportunity to try this theory occurred in relation to the work of the Sulfur Limits Group of the Coordinating Research Council. This group is studying the effect of different concentrations of naturally occurring sulfur compounds in Diesel fuels on engine performance and maintenance. In connection with this program, the Bureau was asked to analyze the fuels for the sulfur types present so that engine performance could be related not only to sulfur content but also to sulfur type. One of the fuels chosen by the Sulfur Limitations Group was from a California crude oil and contained 1.02 percent sulfur. Ten liters of this fuel were percolated through 3-inch by 21-foot silica-gel columns, and 6,700 ml. of an aromatic-sulfur portion was obtained that could be used as a test sample with which to test various silica-gel techniques for their efficiency in concentrating the sulfur compounds by type. Several different diluents and desorbents have been used with variant results. Figure 15 shows specific-gravity, refractive-index, and sulfur-distribution curves based on data obtained from a 900-ml. sample, diluted with 2,700 ml. of n-pentane and charged to a 1-1/2-inch by 21-foot column. The absorbed sample was first desorbed with benzene and then with isopropyl alcohol. The sulfur

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29/ Smith, H. M., Preliminary Report of Studies on the Composition and Physical Properties of Diesel Fuels: Soc. Auto. Eng. Quart. Trans., vol. 3, No. 1, January 1949, pp. 164-177.

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concentration shows a plateau at about 2.2 percent until near the end of the desorption, when it jumped to over 10 percent. Enough data have not been obtained to determine if the various sulfur concentrations represent different types, but the study appears promising.

Jet-Propulsion Fuels

A continuation of the work described in the last annual report on jet-propulsion-fuel analysis has been concerned primarily with freezing-point determinations and possible correlations between this property and composition. One phase of this work involved a microscopic study of 14 samples of jet-propulsion fuels at temperatures as low as -72°F. During this study over 40 photomicrographs were obtained illustrating crystal growth at carefully controlled temperatures, 2 examples of which are given in figure 16. This study is now continuing, with emphasis on determining the effect of prolonged low temperature on various samples with respect to the formation of crystals and tendency to absorb atmospheric moisture.

Utilization

The practical aspects of Diesel-fuel and gasoline research are realized in the utilization of these products. The best bridge between consumer utilization and research data appears to be the fuel test in a small laboratory engine. Toward that end, the Bartlesville laboratory is constantly striving to increase the precision of its testing units and to make complete its coverage of various engine units for different types of fuel.

The Bureau of Mines is continuing active participation in National Exchange Group activities in rating monthly samples of aviation, motor, and Diesel fuels whereby the validity of resulting data obtained on the test engines throughout the country are evaluated. Participation in conferences on operation and maintenance problems that arise in the use of this test equipment also is being maintained. A member of the staff is chairman of the National Exchange Testing Section and leader of the Operation and Maintenance Group serving the Bartlesville local area. As leader of the local group, he represents it as a member of the National Operation and Maintenance Group. These activities, formerly under the jurisdiction of the Coordinating Research Council, were transferred to the American Society for Testing Materials on January 1, 1948.

Gasoline

During the past year, supplementary equipment was procured for converting one of the test units to rating motor fuels by the research method. Thus this unit is used to determine octane numbers of motor fuels by both Motor and Research Methods by means of a minor conversion that can be made in a short time. With this addition, the laboratory is equipped to rate fuels by all five engine methods in current use.

The acquisition of an electronic detonation indicator to supplant the bouncing pin on both motor and research methods is a definite improvement in instrumentation and a material aid in maintaining this test unit in optimum

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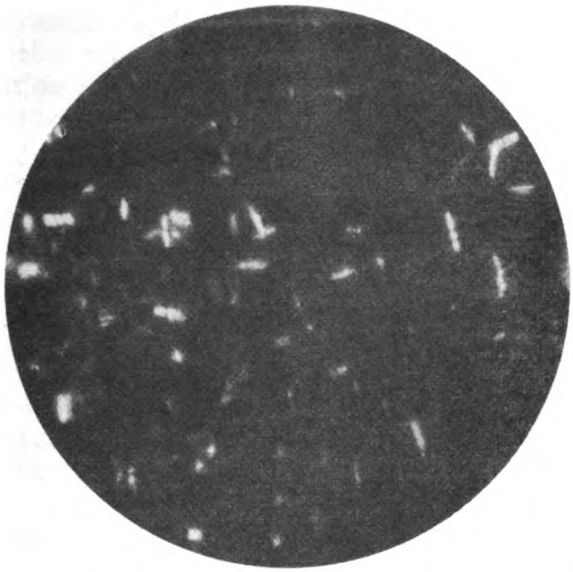
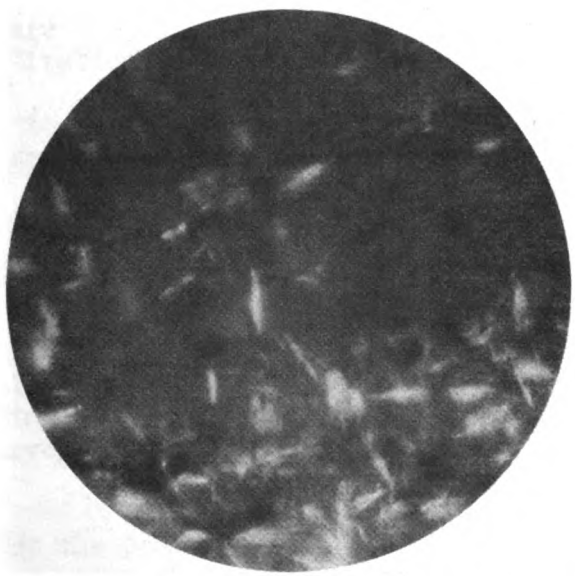


From Bradford crude oil, 572°-617°F. boiling range, 37°F. Federal freezing point, 35°F. initial crystal formation, 32°F. temperature of sample in photomicrograph, cooling rate approximately 0.5°F. per minute, 160X with crossed nicols.



Same as above except + 20°F. temperature of sample in photomicrograph.

Figure 16. - Photomicrographs of wax crystals from a jet-propulsion fuel taken at 20° and 32°F., showing crystal growth at lower temperature.

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condition for measuring knock characteristics of fuels. The installation of voltage stabilizers in the single-phase electric lines that energize the instruments on the engines has materially improved the performance of the instruments and helped the rating procedures.

Since the end of World War II a working group in the Aviation Fuels Division of the Coordinating Research Council, through revisions in equipment and procedure of testing aviation fuels by the laboratory supercharge method, has developed a test method directed toward overcoming the limitations of the present lean-mixture method, improving reproducibility of results in both lean and rich-mixture methods of rating, and including means of evaluating the temperature sensitivity of aviation fuels. The principal objective is to obtain correlation between performance of fuels in full-scale engines in service and laboratory-engine ratings that is not possible with the laboratory test engines in current use.

One of the supercharge engine units is being equipped with modified parts to convert it for operation in rating by the new method designated as the CRC-F21 Method. The Bartlesville laboratory is participating in a group of 15 laboratories assigned the task of determining the reproducibility of ratings of aviation fuels by this method. A program of tests involving six grades of fuels has been formulated, and testing will begin as soon as required new engine parts are available. If development of a method for evaluating fuels in the lean-mixture range of operation results from this work, the limitations of the currently used ASTM D614 Method in rating fuels of high output will have been overcome, and a method suitable for both engine manufacturer and fuel producers' use will have been attained.

Participation in this activity will enable the Bureau to keep abreast of advances in fuel utilization in the aviation field.

Of direct interest to motorists, as well as petroleum refiners and car manufacturers, are the reports on surveys of motor gasolines published twice a year by the Bureau of Mines. This work has been done under a cooperative agreement with the Coordinating Research Council, Inc. Reports have been issued twice yearly since 1936, with the exception of 1942, when the surveys were omitted. The report for the summer of 1947 was published in January 1948.30/

The American Petroleum Institute replaced the Coordinating Research Council as the cooperating agency during 1947 but maintains a similar agreement under which the survey for the winter of 1947-48 was published in July 1948.31/

Both surveys reflect the postwar trend generally toward higher octane values of motor gasolines, even though the average figures for the Nation as a whole did not attain the peak octane numbers of the survey of the winter

30/ Blade, O. C., National Motor-Gasoline Survey, Summer 1947: Bureau of Mines Rept. of Investigations 4248, 1948, 31 pp.

31/ Blade, O. C., National Motor-Gasoline Survey, Winter 1947-48: Bureau of Mines Rept. of Investigations 4354, 1948, 31 pp.

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of 1945-46. The following tabulation shows the national average octane values by the motor method for the two surveys made during the fiscal year 1948 and, for comparison, of the four surveys in the 2 years preceding:

Grade of gasoline	Fiscal year 1946		Fiscal year 1947		Fiscal year 1948	
	Summer 1945	Winter 1945-46	Summer 1946	Winter 1946-47	Summer 1947	Winter 1947-48
Premium-price	74.9	80.9	78.3	78.5	79.2	79.4
Regular-price	69.7	75.9	74.4	75.0	75.1	75.3

The reports also give data on gravity, corrosion, sulfur content, gum, T.E.L. (tetraethyllead), research octane number, Reid vapor pressure, and distillation analysis.

Figure 17 shows the trend of octane numbers, vapor pressure, and three-distillation temperature points for the two grades of wintertime motor fuel for the past 4 years.

The aviation-gasoline survey initiated last year in cooperation with the Coordinating Fuel and Equipment Committee of the Coordinating Research Council (C.R.C.) has continued. The first report of this series has been issued,[32] the second is at present in press, the third has been completed and sent to the C.R.C. committee for criticism, and samples for the fourth survey are currently being received.

The work of the Bureau of Mines in these surveys consists of two phases: (a) Compilation of inspection test data furnished by the cooperating manufacturers for their products; and (b) determination of laboratory data, previously obtained by the National Bureau of Standards, on certain characteristics of the gasoline related to vapor-lock problems.

The first group of inspection data consists of the following: Octane number, performance number, tetraethyllead content, dye color, distillation range, Reid vapor pressure, copper-dish residue, accelerated gum, heat of combustion, aniline point, specific gravity, aniline gravity constant, freezing point, copper-strip corrosion, and sulfur content. The special data determined by the Bureau of Mines include precision vapor pressure, density at 60° and 70° F., distillation range by method A.S.T.M. D-216 (modified), and viscosity at 70° F. Table 3 summarizes some of the important data from the last three surveys.

Diesel Fuel

The cetane-number test engine was provided with means for obtaining ratings on samples of small volume - approximately 100 milliliters. This technique was devised to obtain cetane numbers of some samples that were too small in volume to permit ratings by the standard cetane method. A report on the device was published[33] in Petroleum Processing, February 1948.

32/ Holliman, W. C., Barker, M. G., and Potts, Nancy, Survey of Commercial Aviation-Gasoline Characteristics - March 1947 Production: Bureau of Mines Rept. of Investigations 4273, 1948, 16 pp.

33/ Chase, J. O., and Puckett, A. D., Modified Procedure Reduces Sample Size for Routine Cetane Number Determination: Petrol. Processing, vol. 3, 1948, p. 120.

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	Winter	Motor Octane No.	Research Octane No.	R.V.P., lb.	10% evap., °F.	50% evap., °F.	90% evap., °F.
Premium-price gasoline	1944-45	75.1	80.5	9.0	132	241	348
	1945-46	80.9	87.7	10.0	123	218	326
	1946-47	78.5	85.0	10.1	124	220	327
	1947-48	79.4	86.2	10.2	124	218	327
Regular-price gasoline	1944-45	70.2	74.2	9.2	133	245	348
	1945-46	75.9	81.7	9.8	125	229	338
	1946-47	75.0	80.1	10.1	125	227	334
	1947-48	75.3	80.2	10.1	126	229	335

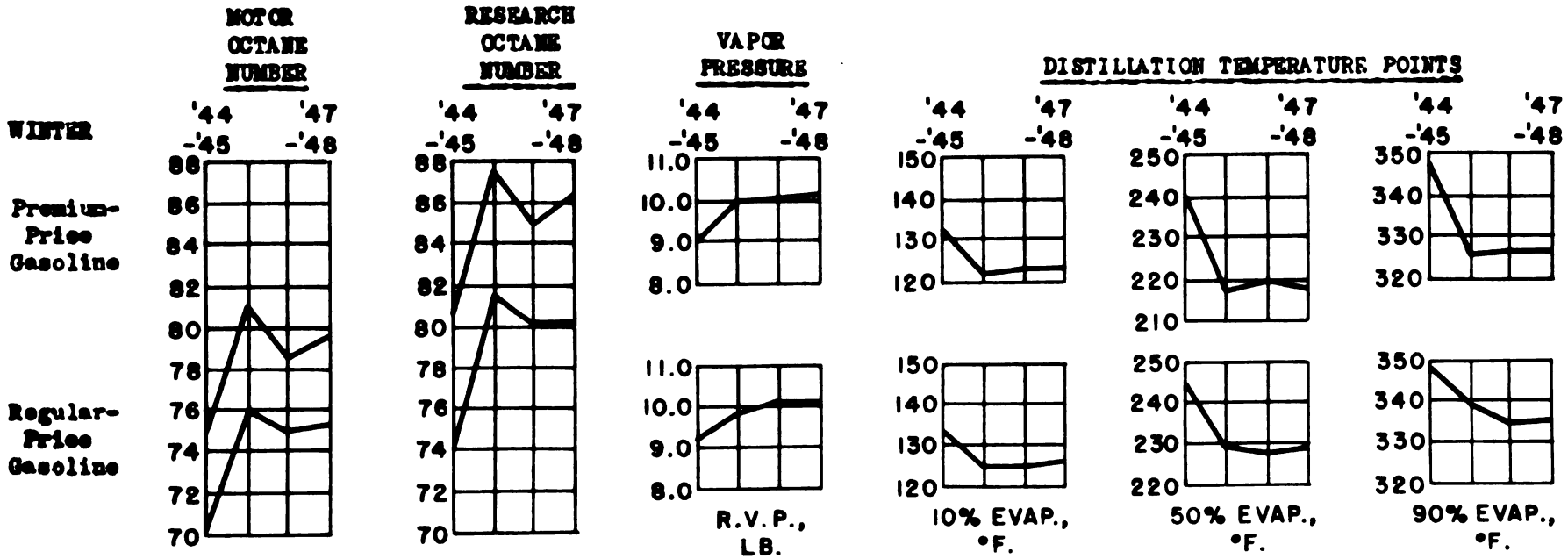

Figure 17. - Summary of data for motor-gasoline surveys for winters of 1944-45 to 1947-48.

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TABLE 3. - Summary of data for aviation gasoline from the 1947 and 1948 surveys

Test	Grade 80			Grade 91/98		
	March 1947	July 1947	Jan. 1948	March 1947	July 1947	Jan. 1948
Octane No.:						
Lean mixture.....	80.4	80.5	80.3	93.3	93.0	92.8
Rich mixture.....	-	-	-	98.6	98.9	98.6
Performance No.:						
Lean mixture.....	-	-	-	-	-	-
Rich mixture.....	-	-	-	-	-	-
Reid Vapor Pressure, pounds..	6.4	6.3	6.6	6.5	6.3	6.5
D-86 distillation temperature °F.						
90% evaporation.....	242	238	236	241	240	233
Sum 10+50.....	345	346	336	347	348	341
Specific gravity, 60°/60° F..	0.705	0.705	0.706	0.710	0.712	0.712
Viscosity, kinematic, 70° F., cs.	0.604	0.603	0.592	0.606	0.606	0.592

Test	Grade 100/130			Grade 115/145		
	March 1947	July 1947	Jan. 1948	March 1947	July 1947	Jan. 1948
Octane No.:						
Lean mixture.....	iso+ 0.15	iso+ 0.16	iso+ 0.13	-	-	-
Rich mixture.....	-	-	-	-	-	-
Performance No.:						
Lean mixture.....	105.9	106.1	105.1	118.2	117.9	117.6
Rich mixture.....	130.9	131.2	130.7	148.0	146.8	145.8
Reid Vapor Pressure, pounds..	6.3	6.3	6.5	6.3	6.5	6.5
D-86 distillation temperature °F.						
90% evaporation.....	246	246	244	243	245	250
Sum 10+50.....	358	355	350	359	358	356
Specific gravity, 60°/60° F..	0.702	0.703	0.704	0.701	0.701	0.700
Viscosity, kinematic, 70° F., cs.	0.615	0.618	0.605	0.616	0.613	0.606

An additional test unit for rating Diesel fuels, delivered at the station as the fiscal year ended, consists of the standard cetane test engine provided with a DC dynamometer of 15-hp. capacity, which can be operated at any desired speed up to 4,500 r.p.m.

As the trend in the Diesel power field continued toward the development of engines of progressively higher rotational speeds and greater power output for given size and weight, the need for evaluating the combustion characteristics of the fuels suitable for such engines undoubtedly will require additional means for measuring combustion phenomena occurring in the process of power generation beyond that possible in the present standard cetane test

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unit, which measures ignition delay at a speed of 900 r.p.m. In addition to determining ignition lag of the fuel sample, this Diesel research unit will permit measurement of the power generated by the engine and thereby provide another basis for comparing test samples with standard reference fuels, thus presenting means for supplementing and augmenting the cetane rating scale, which has already proved inadequate to cover the range of superfractionated samples produced in the Diesel-fuel studies described previously.

The motor-generator set transferred from the San Francisco laboratory will provide the electric current for energizing the DC dynamometer. The versatility of this research unit makes it one of the most important additions to the engine laboratory, in that it will serve for a variety of test applications to yield other data on combustion phenomena that will be required as the art of rating fuels for their optimum utilization progresses. In short, this equipment is much less likely to become obsolete than are some of the test engines in current use.

Ignition Bomb. - Development work was continued on a constant-volume bomb to be used for determining the ignition quality of small samples of fuel. This test unit, exclusive of instrumentation, consists of: (1) The combustion bomb, a stainless-steel pressure vessel with a volume of about 16.5 cubic inches; (2) a furnace designed to house and heat the bomb, yet allow ready access to several openings into the bomb shell; (3) a fuel injector that houses directly into one end of the bomb; (4) a fuel-injector pump; and (5) suitable air-charging and fuel-handling controls. Instrumentation for the lay-out consists of: (1) Triggering circuits to initiate fuel injection and begin the measurement and recording cycle; (2) a rate-of-pressure-change indicator or balanced pressure indicator connected into the combustion space and giving an electrical output proportioned to the pressure phenomena measured; (3) an electrical system to indicate time of injection; (4) an oscillator to provide timing reference marks; and (5) a cathode-ray oscillograph into which the aforementioned electrical impulses are fed to give the complete time-base diagram of fuel injection and subsequent combustion. This diagram will show injection delay; and, if the rate-of-pressure-charge indicator is used, other combustion performance values, such as peak acceleration of pressure.

Work on this project has progressed to the point that the bomb cell, injection system, and associated components have been completed; the furnace has been completed and fitted with automatic temperature control; and instrumentation has been essentially completed. Preliminary tests have demonstrated that the furnace will operate properly and maintain the desired bomb temperatures within a few degrees variation; the injection system has been tested and found satisfactory for beginning tests; and the instrumentation has been tested sufficiently to indicate that its performance will be satisfactory.

It is intended that the unit first will be used to investigate fuels for correlation between ignition lag in a constant-volume bomb and cetane number as determined by the A.S.T.M. Method. If a relationship is established satisfactorily, this equipment should prove to be a valuable tool in investigations regarding combustion characteristics of pure hydrocarbons which are available only in very limited quantity.

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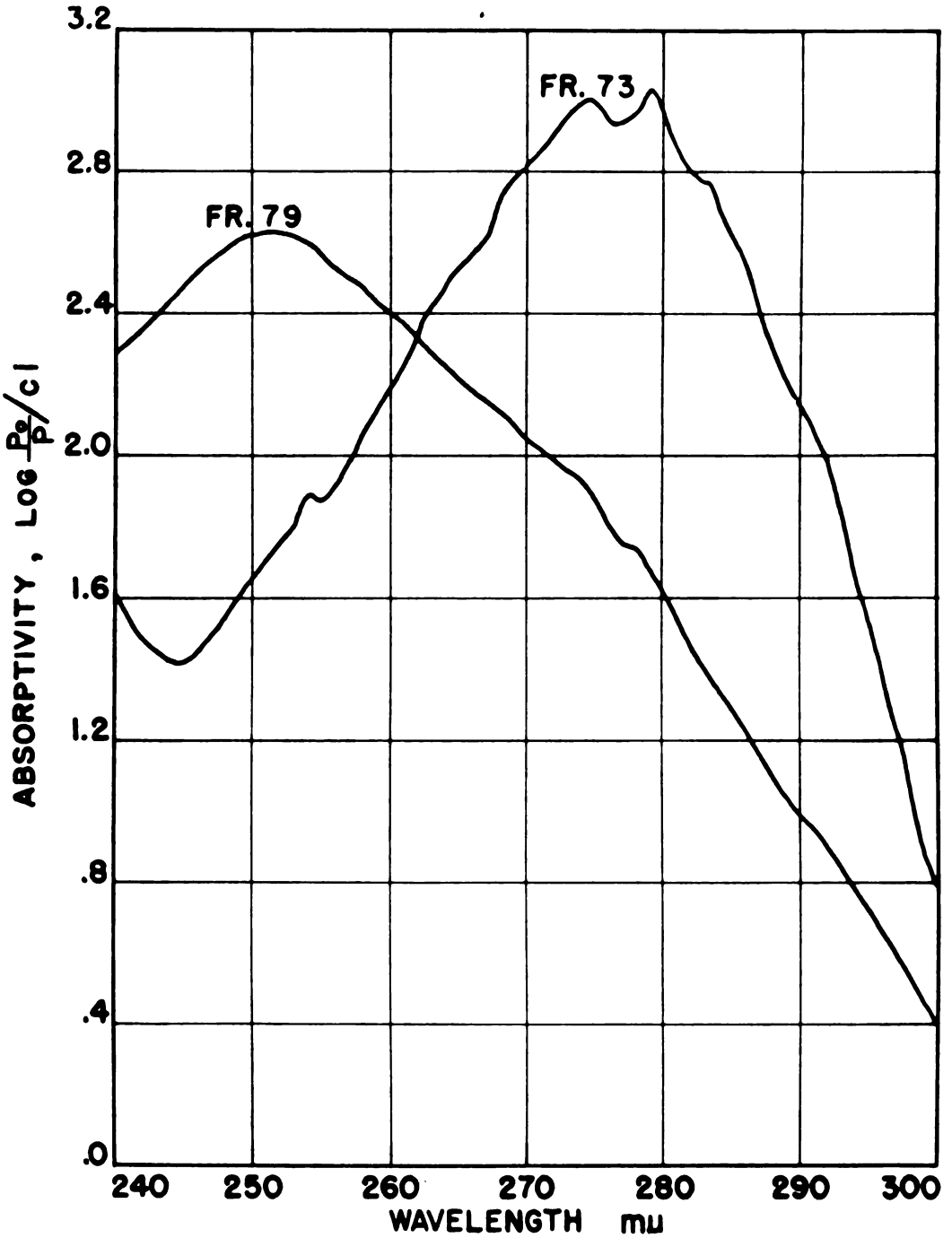

Figure 18. - Ultraviolet absorption curves for Diesel fractions from West Edmond, Okla., crude oil, showing change in composition as distillation proceeds.

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Analytical Methods and Property Determinations

The distinction between analytical methods and property determinations is often very small, as many times the determination of the property is the basis for an analytical method. Thus, the determinations of physical and chemical properties of hydrocarbons constitute the most important part of hydrocarbon analysis. While in the past the Bureau has depended to a considerable extent upon certain properties, such as density and refractive index, current work is tending to develop wider horizons; and optical methods, particularly ultraviolet and infrared spectra, are being used more and more.

An effort is being made to use ultraviolet absorption in the analyses of the Diesel-fuel fractions. Figure 18 shows the type of data obtained, being the absorption spectra of fractions 73 and 79 of the West Edmond distillation. The position of these fractions on the distillation curve may be seen in the previously cited figure 11. Paraffins and naphthenes do not absorb ultraviolet light and give no spectra, so these curves represent only the absorption of the aromatic compounds present. There is considerable change in the type of aromatic compounds between fractions 73 and 79. The double absorption peak for fraction 73 at approximately 277 millimicrons indicates the presence of monocyclic or benzene series compounds, while the single absorption maxima for fraction 79 at 250 millimicrons indicates an entirely different aromatic compound, probably one having two benzene rings. The difference in the molecular structure of the compounds producing these two types of absorption curves affects the physical properties of the fractions correspondingly. This is seen in figure 11, where fraction 73 has a definitely higher cetane value than fraction 79. Thus the conclusion could be reached that the compound in fraction 73 giving rise to the ultraviolet absorption peak at 277 millimicrons yields a high-cetane-number fuel, whereas a compound whose absorption curve has a peak at 250 yields a fuel of lower cetane value. This conclusion would have to be tempered by the knowledge that the absorption curve is on the whole fraction and that paraffin and naphthene types of material also present in the fraction show no absorption at this wave length but do contribute to cetane numbers. It is hoped that the study of absorption data such as the above will yield considerable insight into the composition of a fuel and the causes for it being a good or poor Diesel fuel.

The National Bureau of Standards, in cooperation with the American Petroleum Institute, is developing a library of infrared and ultraviolet curves of hydrocarbons and other organic compounds found in, or related to, natural petroleum. The Bartlesville Station has become a contributor to this library and has submitted infrared and ultraviolet curves for two compounds, one (cyclooctatetraene) purified here, the other (thiophene) purified at the Laramie Station. The cyclooctatetraene, which originated in Germany, was purified at the Bartlesville Station by distillation and freezing. In addition to the infrared and ultraviolet data, thermodynamic data and miscellaneous physical properties, such as density and viscosity, were determined and will be the subject of at least two forthcoming papers. The Bartlesville Station has also been cooperating with Subcommittee XXV of A.S.T.M. Committee D-2 in developing a method for determinating benzene and toluene in gasoline by means of ultraviolet spectra; as a result of this subcommittee's work, an excellent method will shortly be published by A.S.T.M.

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Other A.S.T.M. cooperative work relates to standardizing a method for determining the refractive index of petroleum products in the Bausch & Lomb precision-type and Abbe-type refractometers. This program involves calibration of refractometers with various glass and liquid standards, certified at the Bureau of Standards as to refractive index. It is hoped that a much better procedure for determining the refractive index can be evolved from this work.

Another A.S.T.M. project with which the Bartlesville Station has been concerned is the determination of vapor pressure, related directly to the aviation-gasoline survey. In that survey, one of the properties that the Bureau determines is the vapor pressure by a precision method. The A.S.T.M. has been comparing data obtained by this method and by several modifications of the Reid method, with the net result that a procedure for determining the Reid vapor pressure of aviation gasoline has been recommended that will increase the precision of the results.

The silica-gel studies of sulfur compounds make necessary a large number of sulfur determinations. By the present method of analysis, several days elapse after the samples for sulfur content are submitted until the results are reported. To reduce this time lapse, apparatus was set up to determine the sulfur content by burning the sample in a vertical packed tube heated to 1,600°-1,800° F. Vapors from the burned sample are absorbed and titrated to determine the percentage of sulfur present. Several trial runs showed that the procedure checked the currently used bomb method and was much more rapid. Apparatus was ordered and assembled for setting this method as a routine procedure.

General reconditioning of the carbon-hydrogen determination apparatus for light hydrocarbons, set up and perfected by M. C. Simmons,[34] a former member of the Bartlesville staff, was begun. Carbon-hydrogen analyses are intended as an aid in interpretating data in the various investigations under way. This apparatus followed essentially the normal method for combustion analysis, except for some improvement in weighing procedure to increase accuracy and a radical change in sample introduction. The latter improvement lay principally in a special lamp for burning the sample from a wick after which the products of combustion were led into the conventional combustion train for complete conversion to carbon dioxide and water. In the present Diesel-fuels program, heavier hydrocarbons are studied more often than lighter ones, and for these heavier samples the wick lamp fails. In addition the wick-type lamp requires quite careful regulation of the "primary" and "secondary" air. To avoid these difficulties, a new type of lamp has been designed and is now under investigation. This lamp involves a hypodermic syringe type of fuel injector which should avoid the difficulties inherent in the wick-type lamp - that is, the precise air regulation necessary to maintain a flame burning from a wick. It should also accommodate any weight of fuel that can conveniently pass through the hypodermic needle and be ejected from the nozzle. In trial runs the highest-boiling sample obtained in the

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[34] Simmons, M. C., Determination of Carbon and Hydrogen in Petroleum Distillates: Anal. Chem. vol. 19, 1947, pp. 385-389.

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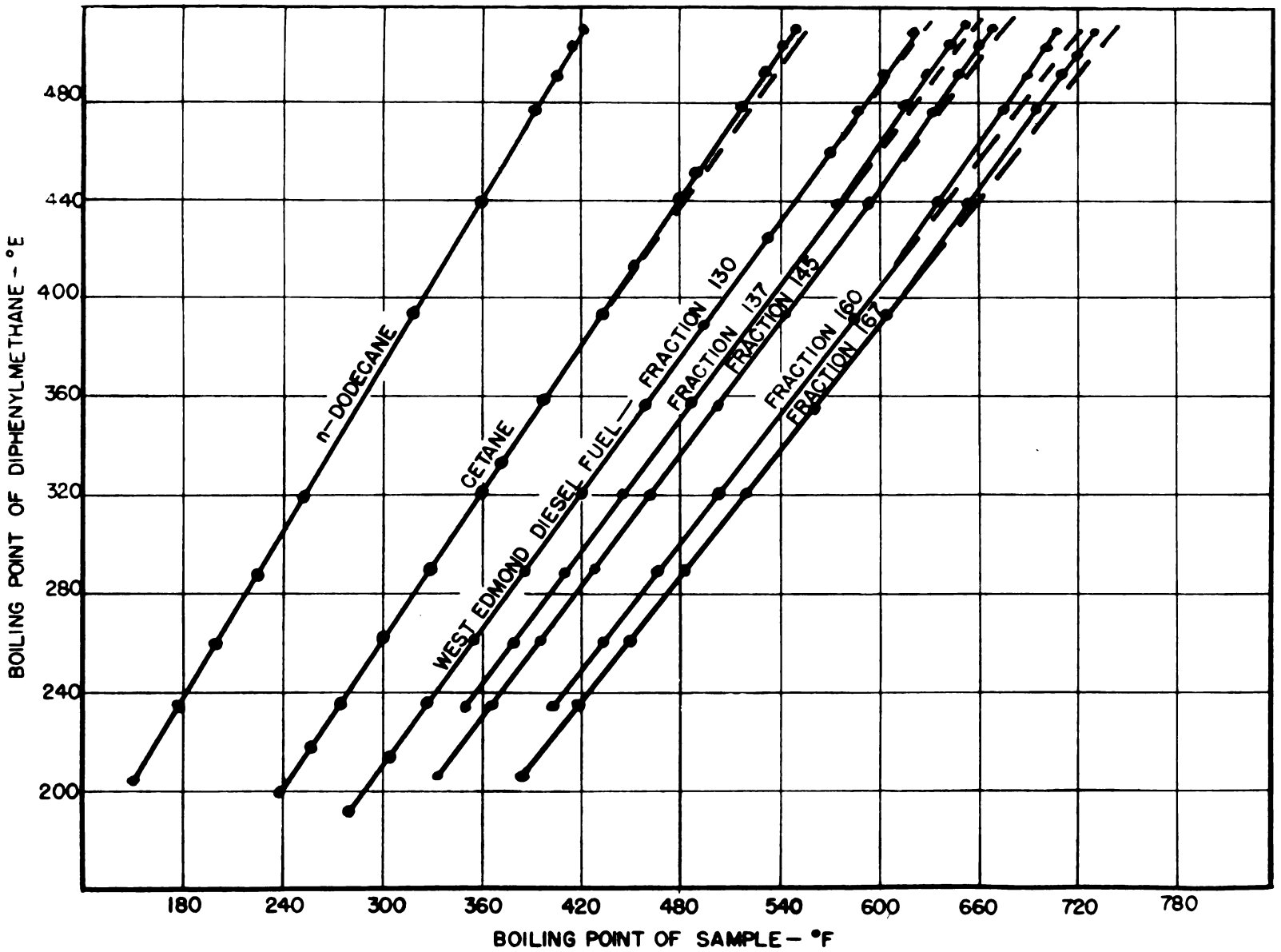

Figure 19. - Relationship of boiling points at low pressures of unknown hydrocarbons and Diesel fractions versus boiling point of diphenylmethane.

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West Edmond crude-oil investigation (fraction 167, B.P. 748° F., viscosity at 37.8° C., 17.885 centistokes) has been burned from the nozzle, apparently in a satisfactory manner. So far, efforts have been concentrated principally upon the mechanical problems involved in the combustion of the fuel rather than on the recovery of the combustion products. After this first problem is completely solved, the second should be no greater than that involved in conventional carbon-hydrogen combustion trains.

Work on an apparatus and procedure for determining bromine numbers of hydrocarbon distillates by direct electrometric titration was conducted with considerable success. The method tentatively adopted affords a considerable saving in time and material with respect to the A.S.T.M. method and on the basis of over 400 determinations on 200 samples it appears to give comparable results. The mechanics of the method indicate other definite advantages that are in process of investigation.

Work has been initiated on the preparation of apparatus for determining minute quantities of water in hydrocarbon distillates. This equipment is essential in conducting tests to determine tendencies of jet-propulsion fuels to absorb atmospheric moisture at low temperatures, apparently an important deleterious effect from the standpoint of jet-propulsion-fuel-engine operation at temperatures below the freezing point of water.

The vacuum fractionation of samples presents the problem of conversion of the boiling point at reduced pressures to equivalent temperatures at atmospheric pressure so the distillation curve can be continuous from the initial fractionation at atmospheric pressure through the vacuum distillation. Moreover, temperatures at pressures other than that at which the fractionation is conducted are needed for comparison with literature data on hydrocarbons for identification purposes. Conversion charts are available for average values, but these charts in many instances are not accurate for narrow-boiling fractions. To provide more accurate boiling-point data on these fractions, ebulliometers were designed and constructed with which boiling temperatures could be obtained at pressures from less than 1 millimeter of mercury to atmospheric pressure if the hydrocarbon samples did not reach cracking temperatures during the determinations. It has been found that the boiling points of a compound determined at several different pressures will plot as a straight line against the boiling points at the same pressure of a compound of similar chemical structure. To have standards for which boiling-point-pressure relationships are known, the boiling points of diphenylmethane (an aromatic-type hydrocarbon) and cetane (a paraffin-type hydrocarbon) were determined very accurately at a series of pressures from below 1 millimeter of mercury to atmospheric pressure. Figure 19 shows the boiling points of n-dodecane, cetane, and several high-boiling fractions from the West Edmond fractionation plotted against the boiling points of diphenylmethane at various pressures. Such plots exhibit linear relationships up to a temperature of about 500° F.; in this region, the data begin to deviate upward from a straight line. This deviation is attributed to erroneous boiling points caused by cracking of the sample. The true atmospheric boiling points of the samples are taken to be the temperature at which extension of a straight line through the lower boiling points intersects the atmospheric boiling-point temperature of diphenylmethane.

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In the various stages of processing the fractions from crude oil, it might be anticipated that in some of the closely fractionated fractions solid hydrocarbons would appear. This has occurred in the case of the West Edmond crude oil, and naphthalene has been found and identified in fraction 39 of the Diesel-fuel distillation and 2,6-dimethylnaphthalene in fraction 69. Figure 20 is from a contribution[35/] from the Bartlesville laboratory in which the details of some of this work have been reported. The figure gives the ultraviolet absorption curve of the 2,6-dimethylnaphthalene isolated from West Edmond crude oil in comparison with a similar curve for a purified commercial sample of the same hydrocarbon. From the positions of the absorption bands on the wave-length axis the two hydrocarbons obviously are identical. Other solid hydrocarbons have also appeared in the course of the investigation into Diesel fuels from crude oil, and positive identification of these will proceed with other work.

Sulfur in Petroleum

With increasing demand on the Nation's crude-oil supplies, greater interest in the problem of refining high-sulfur crude oils is apparent. The Bureau of Mines continued its program of fundamental research on sulfur compounds occurring in petroleum. Much of this program is located at the Laramie Station.

A literature survey to obtain best values of physical properties of the sulfur compounds in petroleum has been continued. This survey involves finding the values reported in the chemical literature for each of the physical properties and selecting the most probable value from these data. Tables have been prepared listing refractive indices for various wave lengths of light, surface tensions, viscosities, refractivity intercepts, specific dispersions, specific refractions, and parachors. In addition, a set of tables previously published, giving boiling points, freezing points, refractive indices, and densities has been revised to include new data published up to January 1, 1948. Apparatus for the determination of purity by the freezing-point method is shown in figure 21.

The survey has revealed that the meager information concerning sulfur compounds found in the literature is often inaccurate. Accordingly, it is important that the compounds be prepared and purified so that accurate properties may be determined. Compounds that have been purified include thiophene, 2-thiabutane (methyl ethyl sulfide), and 3-thiapentane (ethyl sulfide). The physical and thermodynamic properties of these compounds are being determined in Bureau laboratories.

In the development of new instrumental methods of analysis, such as infrared, ultraviolet, and mass spectrometry, pure compounds are needed for calibrating the instruments and for developing methods of analysis. To assist in filling this need, a cooperative agreement has been made with the National Bureau of Standards whereby samples of purified sulfur compounds are transferred

35/ Hopkins, R., and Adams, N. G., The Isolation and Identification of 2,6-Dimethylnaphthalene from West Edmond Crude Oil: Proc. Oklahoma Acad. Sci., vol. 28, 1948, pp. 85-89.

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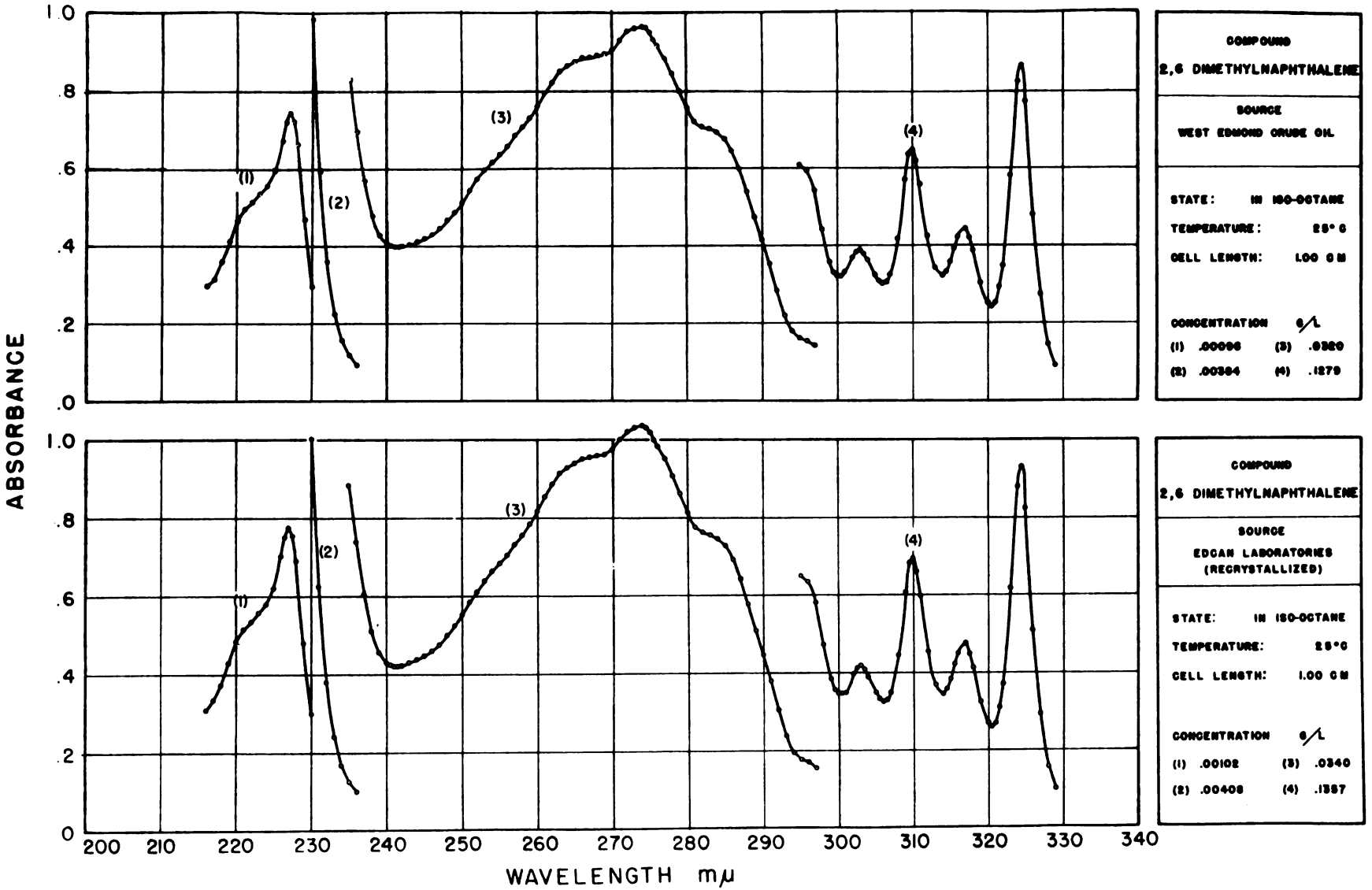

Figure 20. - Comparison of ultraviolet absorption spectra of 2,6-Dimethylnaphthalene from two independent sources - one from a crude oil and the other a synthetic sample.

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Figure 21. - Apparatus for determining purity by freezing-point method.

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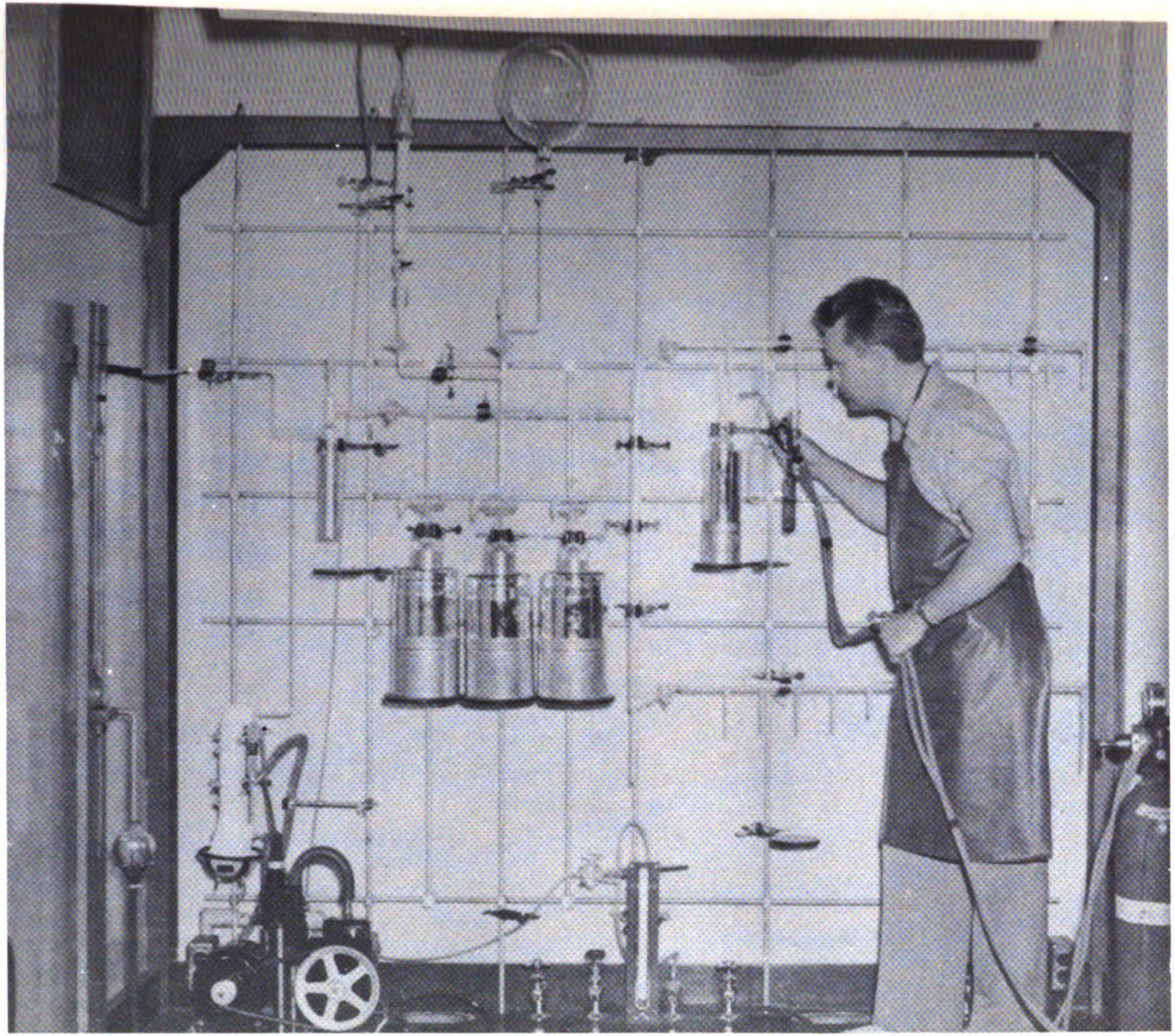

Figure 22. - Apparatus for bottling purified sulfur compounds "in vacuum."

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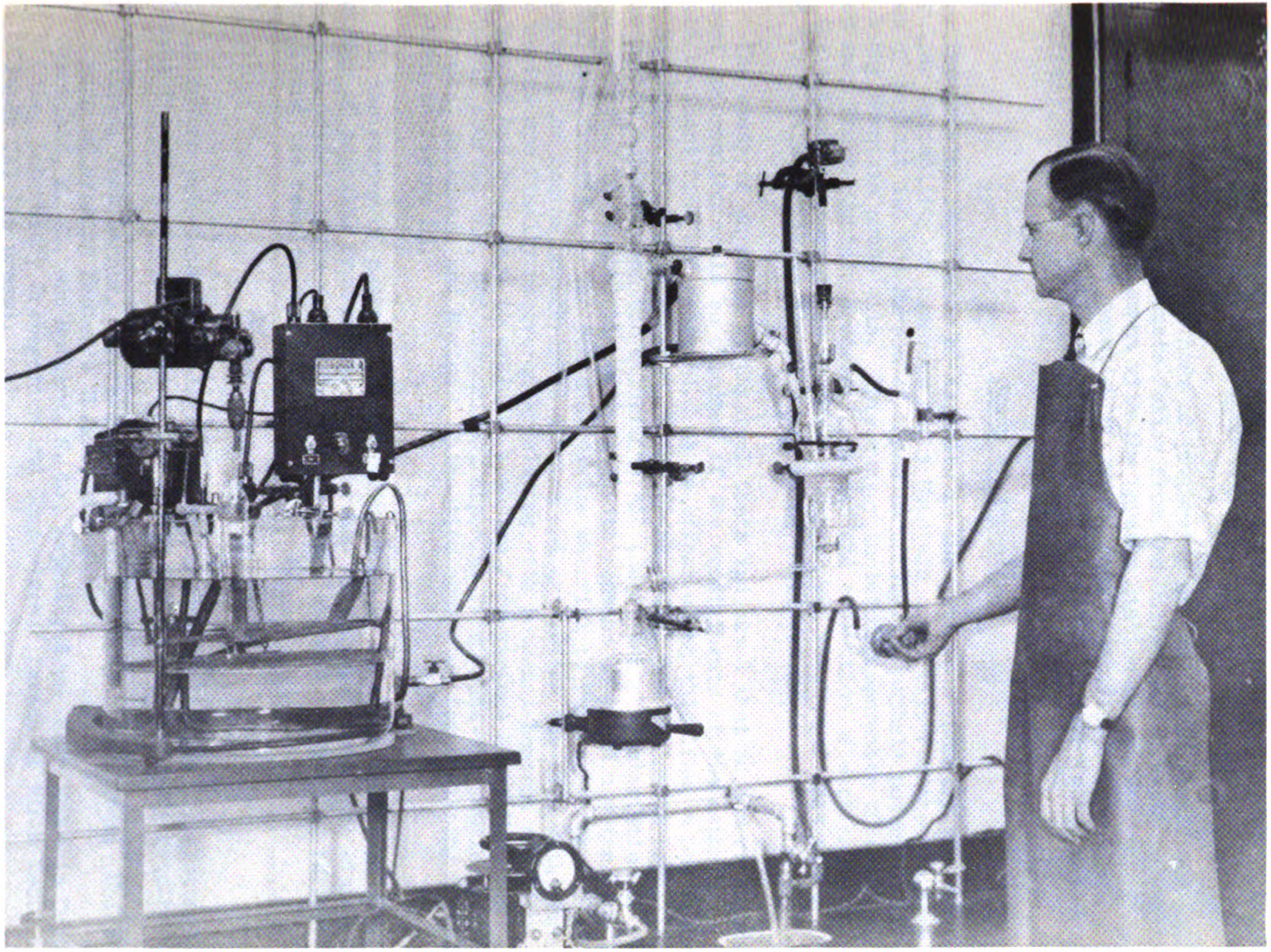

Figure 23. - Extraction apparatus for analyzing asphalts.

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to the Bureau of Standards for bottling and distribution to interested laboratories. The three compounds listed above have already been delivered to the Bureau of Standards. Figure 22 shows the apparatus used by the Bureau of Mines for bottling purified sulfur compounds.

An investigation of methods of preparaing unsymmetrical disulfides has been carried out by a graduate fellow from the University of Wyoming, working under a cooperative agreement with the Laramie Station of the Bureau. This study[36] involved the preparation of two unsymmetrical disulfides, 2,3-dithiapentane (methyl ethyl disulfide) and 3,4-dithiaheptane (ethyl n-propyl disulfide).

Study of Asphalts

The growing importance of asphalts in the petroleum industry and the peculiar suitability of numerous Rocky Mountain crude oils for the preparation of asphalt led the Bureau of Mines to survey the asphalt potentialities of Rocky Mountain crude oils. This survey included preparation of asphalts from many Rocky Mountain crude-oil sources and evaluation of such asphalts by the methods in common use by the industry. The results of this survey and the testing of these asphalts are being published.[37]

The study of asphalts by physical tests indicated that much more fundamental information could be obtained if the constituents of the asphalt could be identified and measured. As an effort along this line, a new method was developed for determining asphaltenes, oils, and resins in asphalts.[38] This method depends upon the solubility and adsorption characteristics of the three groups. The asphalt is extracted with pentane to yield a petane-insoluble asphaltene fraction. The pentane-soluble material is further separated by adsorbing the resins on anhydrous alumina and extracting the oils with pentane. The resins are finally recovered by eluting with methanol-benzene solution. The method has been used to evaluate asphalts from various Rocky Mountain crude-oil sources and, for comparison, asphalts from crude-oil samples from California, Arkansas, and Mexico. Extraction apparatus for analyzing asphalts is shown in figure 23.

In the survey of petroleum asphalts from Rocky Mountain crude-oil sources, a number of asphalts from native bitumens and bituminous sands were examined. The usual asphalt tests were made on these samples, and a report is in preparation giving the results of this work.

THERMODYNAMICS OF PETROLEUM

In modern petroleum technology, the efficient functioning of existing refining processes and the development of new methods of treatment require

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36/ Maticka, Jack Barney. Preparation of Unsymmetrical Disulfides. University of Wyoming Master's Thesis, May 1948.

37/ Stanfield, K. E., and Hubbard, R. L., Asphalts from Rocky Mountain Crude Oils, Laboratory Preparation and Comparison: Bureau of Mines Tech. Paper 717 (in press).

38/ Hubbard, Rethel L., and Stanfield, K. E., Determination of Asphaltenes, Oils, and Resins in Asphalt: Anal. Chem., vol. 20, 1948, pp. 460-465.

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exact knowledge of the thermodynamic properties of the many hydrocarbons and related substances occurring in petroleum. In the absence of thermodynamic data for any particular group of hydrocarbons of interest, no estimate whatsoever can be made of the necessary conditions of temperature and pressure required to give efficient, economic operation of a proposed process. A lack of data either will prevent progress or will necessitate expensive trial-and-error research.

Recognizing the need for accurate data, the Bureau of Mines is carrying on a systematic program of thermodynamic research which includes the following related lines of investigation: (1) Low-temperature calorimetry; (2) vapor-heat capacity and heat of vaporization; (3) heat of combustion; (4) vapor pressure; and (5) calculation of thermodynamic functions by statistical methods. The data provided by these various investigations yield numerical values of the "free energy" for any proposed chemical process. The free energy is a measure of the driving force of a chemical reaction. First, it tells the person who is versed in the science whether or not a process is feasible at all and, second, what conditions of temperature and pressure will produce the most economical results.

Each of the five projects has been active during the past year. A brief statement of the work accomplished in each field follows:

Low-Temperature Calorimetry

This work involves measurement of the heat capacities of pure hydrocarbons over the temperature range 11°K. (440° below zero F.) up to a little above room temperature. Heat of transition and heat of fusion are determined when necessary. From these measurements, values of the entropy for the compound may be evaluated. This thermodynamic property (entropy) is absolutely necessary for carrying out the free-energy calculations referred to above.

During the year a second adiabatic calorimeter has been built and put into operation, greatly increasing the efficiency and convenience of the work.

A study of the heat capacity of benzene[39] was carried out. Rather strangely, a completely reliable series of measurements on this extremely important compound had not previously been made. The present work has given an assured value of the entropy of benzene.

A complete thermal study of a family of six similar hydrocarbons known as the C_7H_{14} alkylcyclopentanes was completed. The results of this investigation were presented before the American Chemical Society at the Chicago meeting in April 1948[40] and will be valuable in research involving production of these substances or their utilization in new processes.

39/ Oliver, G. D., Eaton, Margaret, and Huffman, H. M., Heat Capacity, Heat of Fusion and Entropy of Benzene: Jour. Am. Chem. Soc., vol. 70, 1948, pp. 1502-1505.

40/ Oliver, G. D., Eaton, M., and Huffman, H. M., Low-Temperature Thermal Data on the C_7H_{14} Alkylcyclopentanes: Abs. of Papers, 112th Meeting, Am. Chem. Soc., Chicago, April 1948.

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A number of other hydrocarbons have been studied and the results made available to industry through project 44 of the American Petroleum Institute at the National Bureau of Standards. These include cyclohexene, cyclopentane, n-heptane, 2,2-dimethylpentane, and hexamethylethane. A hydrocarbon of considerable interest and potentially great importance in chemical manufacturing has been studied. This is cyclooctatetraene (or COT). Limited production was found by our science search teams in Germany after World War II, and several of the Nation's large chemical companies now are taking an active interest in this substance.

By invitation the role played by this type of research was summarized[41] before the American Chemical Society as part of a program given by nationally known scientific leaders.

Vapor Heat Capacity and Heats of Vaporization

The results of low-temperature calorimetry provide entropy values for solids and liquids. These data, together with a knowledge of heat of vaporization and the heat capacity of vapors, give information about the thermodynamic properties of vapors. Since many industrial processes involve gases, this sort of information is a necessary part of the thermodynamic picture.

During the past year a study of the five different hexanes occurring in petroleum was completed. These data enter into processes for developing special aviation fuels. A portion of this information has been published in a chemical journal,[42] while other data from these studies have been included in the tables published by the American Petroleum Institute.

Data have also been obtained for methylcyclopentane, 1-pentene, 2-methyl-1-butene, and 2-methyl-2-butene. The information on this last compound was the basis of a report delivered before the American Chemical Society.[43]

Combustion Calorimetry

A quantity almost as basic as entropy in carrying out thermodynamic calculations is the enthalpy. This thermodynamic function may be obtained by measuring heats of combustion.

41/ Huffman, Hugh M., The Application of Calorimetric Methods to Hydrocarbon Research; part of a Symposium on Purity and Identity of Organic Compounds: Am. Chem. Soc., 111th Meeting, New York, September 1947.

42/ Waddington, Guy, and Douslin, D. R., The Vapor Heat Capacity and Heats of Vaporization of n-Hexane and neo-Hexane: Jour. Am. Chem. Soc., vol. 69, 1947, pp. 2275-2278.

43/ Scott, D. W., Waddington, Guy, Smith, J. C., and Huffman, H. M., Thermodynamic Properties of 2-Methyl-2-Butene: Abs. of Papers, 112th Meeting, Am. Chem. Soc., Chicago, April 1948.

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The chemical industry now is manufacturing vast quantities of hydrocarbon derivatives, of which chloro compounds are among the most important. For this reason, much effort has gone into solving the difficult problem of measuring the heats of combustion of these chloro compounds. A successful method has been developed, and two papers describing the method and preliminary results have been presented before the American Chemical Society.[44, 45] The successful solution of this problem will open up an extensive territory of fruitful investigation. Several chemical concerns have expressed gratification that this problem is being solved.

Vapor Pressures

Knowledge of the vapor pressure of hydrocarbons and derivatives, over a range of temperature, supplements the other thermodynamic quantities described in a number of ways. Apparatus for measuring this property over two different pressure ranges has been designed, constructed, and successfully tested during the past 12 months. Figure 24 illustrates a portion of this new apparatus. This addition to the research program will prove very valuable as time goes on. An important hydrocarbon derivative containing sulfur (thiophene) has been studied over the pressure range covered by the two methods. Cyclooctatetraene and hydrazine likewise have been studied.

Statistical Mechanical Calculations

Direct measurement is the surest method of determining thermodynamic properties of molecules. However, thermodynamic functions may be calculated for relatively simple molecules using the theoretical methods of statistical mechanics. Spectroscopic and molecular-structure data are necessary for this approach. This method permits evaluation of important thermodynamic functions at temperatures beyond the range of experiment and also yields information as to what goes on "inside molecules."

Work in this field has been active. A paper[46] correlating the results of some vapor heat-capacity measurements and statistical calculations has added to the knowledge of the benzene molecule. Thermodynamic functions for 2-methyl-2-butene, referred to earlier, were calculated from spectroscopic and molecular data supplemented by the results of thermal measurements. Similar results are also available for thiophene, hydrazine, and spiropentane.

Function of Thermodynamics Research

Steady flow of new and reliable thermodynamic data to engineers and research workers is necessary if the methods of refining and processing

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44/ Knowlton, J. W., Hubbard, W. N. and Huffman, H. M., A Technic for the Calorimetric Combustion of Chlorinated Hydrocarbons: Abs. of papers, 112th Meeting, Am. Chem. Soc., Chicago, April 1948.

45/ Hubbard, W. N., Knowlton, J. W., and Huffman, Hugh M., The Heats of Combustion of Chlorobenzene, o-and p - Chloroethylbenzene and p - Dichlorobenzene: Abs. of papers, 112th Meeting, Am. Chem. Soc., Chicago, April 1948.

46/ Scott, D. W., Waddington, Guy, Smith, J. C., and Huffman, H. M., The Contribution of Anharmonicity to the Heat Capacity of Benzene Vapor: Jour. Chem. Phys., vol. 15, 1948, pp. 565-567.

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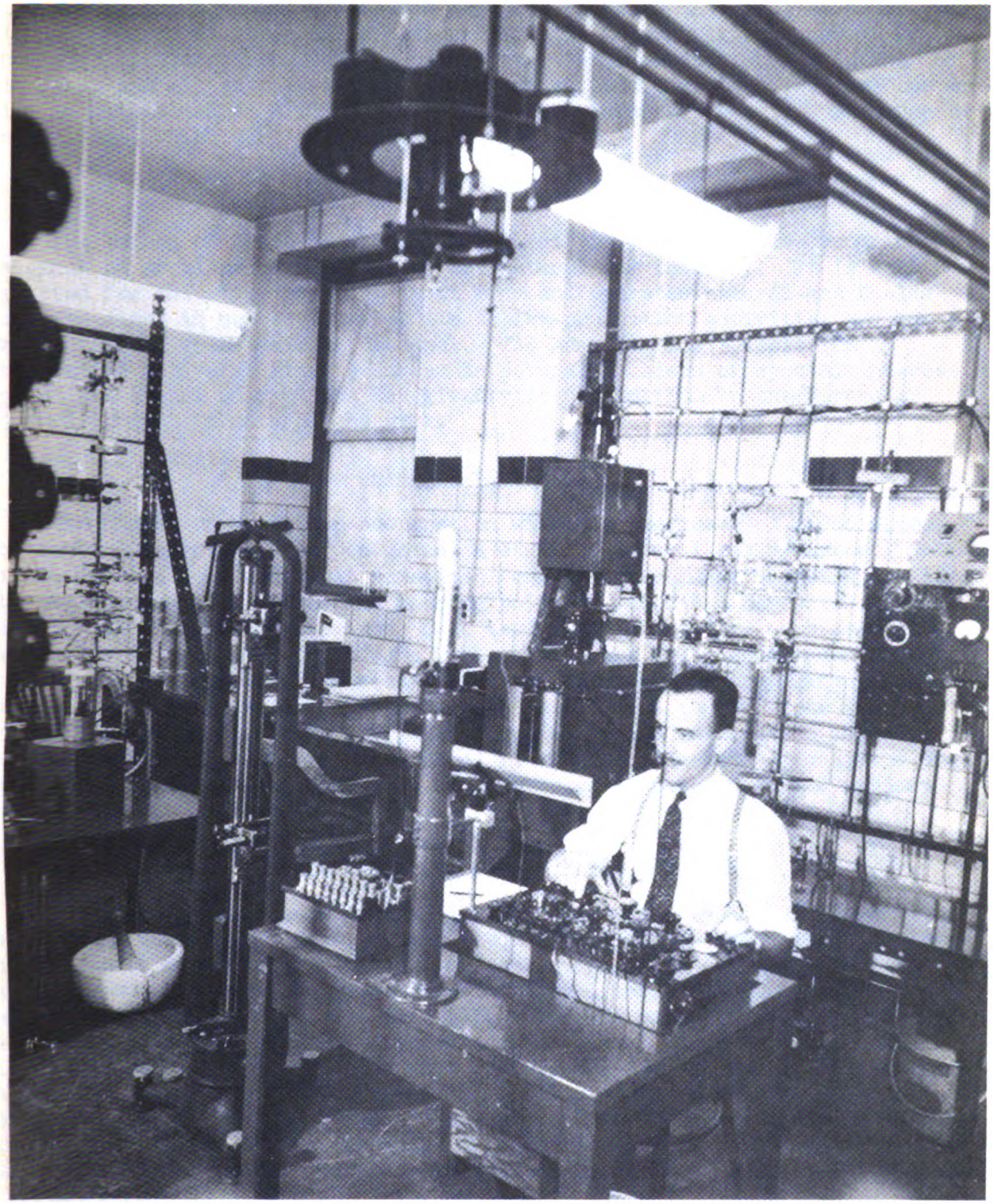

Figure 24. - Apparatus for accurate measurement of vapor pressures.

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petroleum are to advance in future as they have in the past. It is the function of the thermodynamics research group to maintain this flow of data. The planned program of research is designed to fill in conspicuous gaps in the knowledge of hydrocarbons and to anticipate trends of development in the petroleum and allied industries. To obtain maximum efficiency, active cooperation is maintained at all times with all other laboratories, both Government and private, which work in this general field.

TRANSPORTATION OF NATURAL GAS

The Bureau of Mines continued throughout the year an active program of research on problems of interest to the natural-gas industry. It is well-equipped for this type of work, as it owns and operates natural-gas fields and pipe lines in connection with its helium-production activities and has a small staff of well-trained personnel. The American Gas Association is cooperating actively with the Bureau in several problems of special interest and at its annual conventions has given wide recognition to the Bureau's accomplishments in natural-gas work.

Natural-Gas Hydrates

The Bureau of Mines, in cooperation with the American Gas Association, for several years has been conducting a study of natural-gas hydrates - solid, white, icelike compounds that sometimes form in natural-gas transmission lines at temperatures well above the freezing point of water and may entirely stop the flow of gas through the line, even though it is operated at pressures of many hundreds of pounds per square inch. This work was discontinued during the war but subsequently was reactivated to the extent of preparing a summary report of all the results and conclusions obtained in the previous work. This monograph[47] furnishes information needed by the natural-gas industry in solving hydrate problems encountered in transporting natural gas from the gas fields to distant markets. It will serve as a handbook on the subject for natural-gas engineers.

Development of a Water-Content Recorder

Most natural gases are saturated with water vapor when they leave the underground reservoir. Some of this vapor will condense and collect as water in low places along the pipe lines, unless equipment is installed for its partial removal before the gas enters the pipe lines. The Bureau's work on natural-gas hydrates disclosed that this water was responsible for the formation of hydrates and resulting operational problems. As a result of this discovery, many of the companies that operate the long-distance, high-pressure, natural-gas pipe lines have invested millions of dollars in equipment to remove a part of the water vapor from the gas before the gas enters the pipe lines. The ability of the companies to operate their pipe lines successfully during the winter months often depends on continued efficient operation of

47/ Deaton, W. M., and Frost, E. M., Jr., Gas Hydrates and Their Relation to the Operation of Natural-Gas Pipe Lines: Bureau of Mines Mon. 8, 1948, 101 pp.

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the equipment for removing the water vapor. An instrument was developed by Bureau of Mines engineers[48] to test the water content of the natural gas, but this instrument could not give a continuous record. The operating companies have requested urgently an instrument that will record continuously the quantity of water vapor in the gas. As a result, the American Gas Association during the present year entered into a new cooperative agreement with the Bureau of Mines for the purpose of developing a satisfactory recorder for this purpose. The cooperative arrangements were completed during February, and during the ensuing 4 months the work consisted mostly in reviewing work of interest to the problem, and assembling the necessary equipment for testing and developing methods to solve the problem. Some of the equipment already assembled for this work is shown in figure 25.

Flow of Natural Gas in Pipe Lines

One problem on which the Bureau worked during the entire year in cooperation with the American Gas Association was a study of the flow of natural gas in large-diameter pipe lines operating at high pressures and at high velocities. The results obtained in former studies of small lines operating at lower pressures and lower velocities had proved inadequate for predicting the capacity of new large-diameter lines and for calculating the efficiencies of existing lines. Accordingly, in October 1946, the Bureau began to study the flow of natural gas through pipe lines.

The investigation was divided into four main phases:

1. Review of literature and present usage.
2. Studies of fundamentals in the laboratory and on comparatively short sections of pipe lines.
3. Field studies on long pipe-line systems.
4. Correlation of data and development of conclusions.

During the present fiscal year, extensive work was conducted on the second major phase of the project, namely, studies of fundamentals in the laboratory and on comparatively short sections of pipe line.

In the laboratory, the viscosity of various natural gases was determined at both low and high pressures at temperatures ranging from near freezing to about 100° F. Arrangements were made with the National Bureau of Standards to make additional determinations of this type.

An experimental 2-inch pipe line about 100 feet long was constructed in the Government-owned Cliffside gas field near Amarillo, Tex., and furnished with a complete set of pressure- and temperature-measuring stations and auxiliary equipment. Numerous tests were made on this 2-inch line, with very satisfactory results. Flows under extreme conditions could be measured with an apparent error not exceeding about 0.5 percent.

48/ Deaton, W. M., and Frost, E. M., Jr., Bureau of Mines Apparatus for Determining the Dew Point of Gases Under Pressure: Bureau of Mines Rept. of Investigations 3399, 1938, 4 pp.

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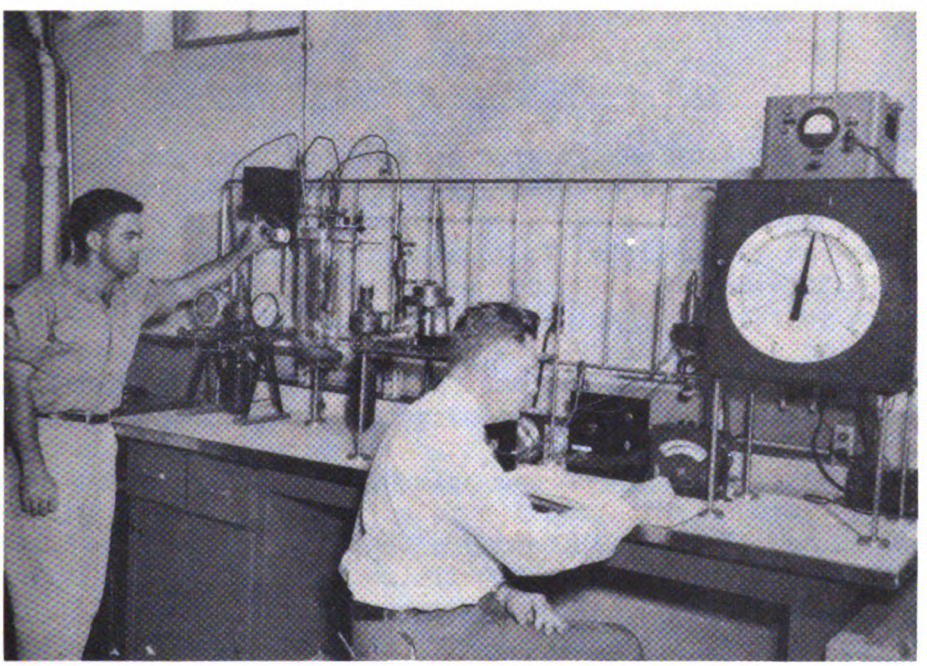

Figure 25. - Laboratory apparatus used in developing water-vapor recorder for use on natural-gas pipe lines.

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During the above field work, approximately 120 feet of 3-1/2-inch O.D. stainless-steel tubing were purchased to continue the work, and arrangements were made with the Naval Gun Factory to bore and hone it on the inside so that the roughness will not exceed sixteen millionths of an inch in height. There are indications that the roughness will not exceed one-half this amount. This honing and polishing will assure at the same time a virtually perfect cylindrical hole in the tube. Special joints were designed to reduce to a minimum any discontinuity of surface at the joints. This tubing will be used in the next phase of field tests on short lengths of pipe. Arrangements also are being made to obtain cameras with electrically operated shutters, so that simultaneous records of all temperatures and pressures may be obtained during the tests, by photographing in one concurrent operation each of the temperature- and pressure-indicating devices. These photographic records will permit making the readings with precision and will afford a permanent record of each reading.

Removal of Nitrogen from Natural Gas

The removal of excess nitrogen from natural gas is another cooperative problem with the American Gas Association that was continued throughout the year. The purpose of this study is to obtain and publish technical data that will assist in the commercial establishment of satisfactory and economical means for removing virtually all nitrogen from natural gases of high nitrogen content. With the increasing market for natural gas at distant markets, the operating companies face the problem either of building more and larger pipe lines, with accompanying compressor stations, or of increasing the heating value of the natural gas being transported through the present lines. The nitrogen in the natural gas will not burn and thus serves only to dilute the burnable constituents. The nitrogen also has a higher specific gravity and is more difficult to move through the pipe lines. The removal of the nitrogen, then, would accomplish a twofold purpose: (1) Permit the moving of a greater volume of gas through the existing pipe lines and (2) increase the heating value of this greater volume of gas. Thus, removal of the nitrogen would accomplish the same purpose as building proportionately more or larger pipe lines, without using the large tonnages of steel and other critical materials that would be required in the pipe lines and compressor stations. The removal of nitrogen would also make marketable some natural gases that cannot now be sold because of the high nitrogen content and resulting low heating values.

The research was begun in February 1947 with a survey of literature relating to gas-separation methods. The preliminary survey indicated that low-temperature processing by liquefying the natural gas and subsequently separating the nitrogen by fractional distillation was the best prospective method for the purpose. Then a pilot plant was built at the Bureau of Mines Exell Helium Plant near Amarillo, Tex., and some preliminary tests were made. Some modifications of the original design were necessary, and as soon as these are completed it is anticipated that acquisition of desired data will begin. The tests will be designed to provide information on the practicability of the method and for the design of large-scale commercial nitrogen-removal plants.

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A paper entitled "Prospective Benefits from Removing Excess Nitrogen from Natural Gas" was presented at a meeting of the Natural-Gas Department of the American Gas Association at Houston, Tex., on May 4-5, and material from the same paper was presented at the association's Production and Chemical Conference in Asbury Park, N. J., on May 24-26. The paper included an appendix giving an extensive bibliography of literature and patent references on gas-separation methods, with particular reference to low-temperature processing.

HELIUM UTILIZATION AND RESEARCH

The Bureau continued throughout the year its aggressive program of research and development leading to continual appraisal of the Nation's helium resources, improvements in processing cycles and equipment, and increasing its utilization through developing new uses and better procedures. The Bureau owns and operates two gas fields and many miles of pipe lines in connection with its helium-production activities, and those facilities, along with the research and development laboratory maintained at the field headquarters station in Amarillo, Tex., offer an ideal situation for research on problems related to the production and transportation of natural gas.

Helium Survey

Helium occurs in natural gases, and there is no other known source for the large quantities of helium required by present-day commercial, military, and Government users. Most natural gases in the United States contain some helium, although the percentage usually is very small, amounting often to only a few hundredths or even a few thousandths of 1 percent. The number of fields that produce commercial quantities of helium, however, are very, very few. The Bureau began a survey of natural-gas fields in the United States in 1917 to locate those containing unusual amounts of helium, and this program has been carried on more or less continuously since that time. Trade journals, drilling reports and other sources of information are checked regularly for new gas fields, extensions of old ones, and wildcat drilling in general, and when gas is encountered in any of these drilling operations, an attempt is made to obtain a sample and analyze it for helium content. By this procedure, the Bureau had located enough helium reserves to meet completely the gigantic expansion program demanded at the outset of the recent war. Only by continuing this careful search will the Government be able to stay abreast of the present demands and future requirements for helium.

Process-Development Research

The increased military and commercial demands for helium have brought also a demand for helium of higher and higher purity. For many years, the Bureau had produced helium of 98.2 to 98.5 percent purity, but this purity has now proved inadequate. During the previous fiscal year, some process-development research was reported in which the helium purity was increased to 99.8 percent or better by passing it through activated coconut charcoal at temperatures ranging from -50° F. to -300° F., and a pilot plant was built to test the process on a commercial scale. The pilot plant was successful. During the present fiscal year, steps were taken to procure equipment for the

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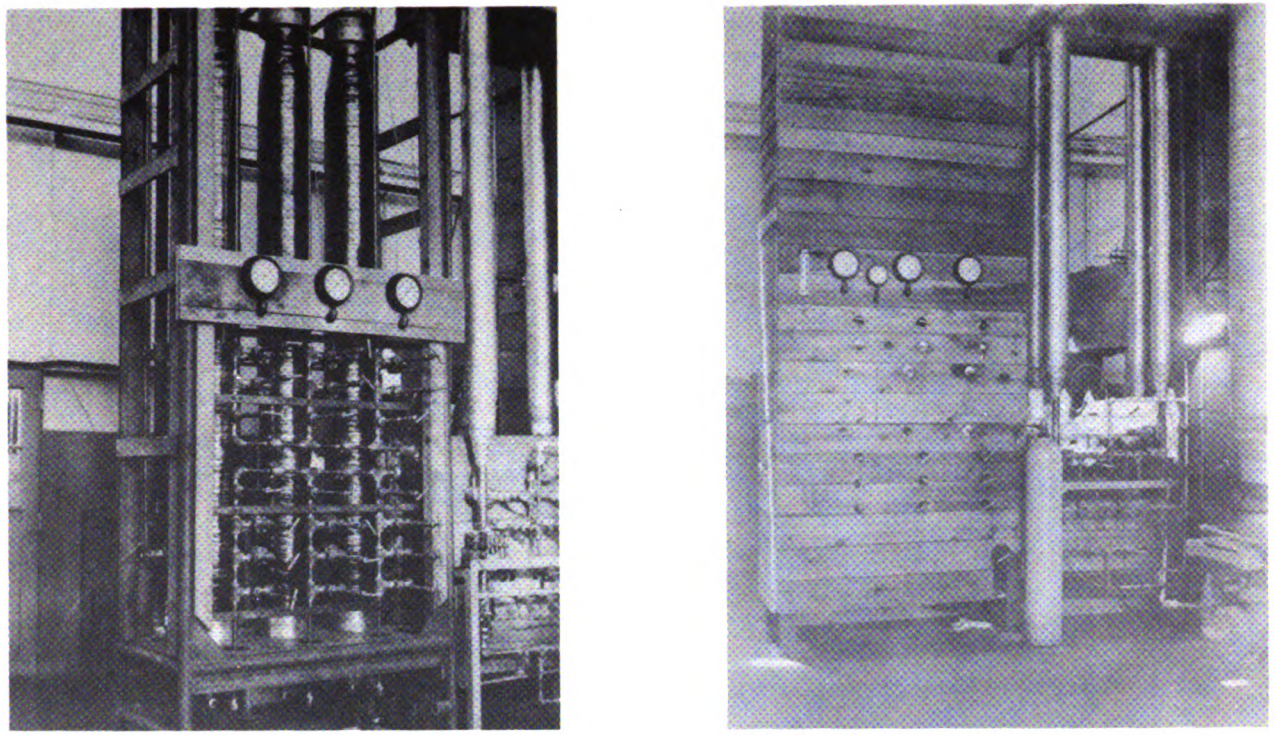

Figure 26. - Charcoal-filled absorbers for helium purification.

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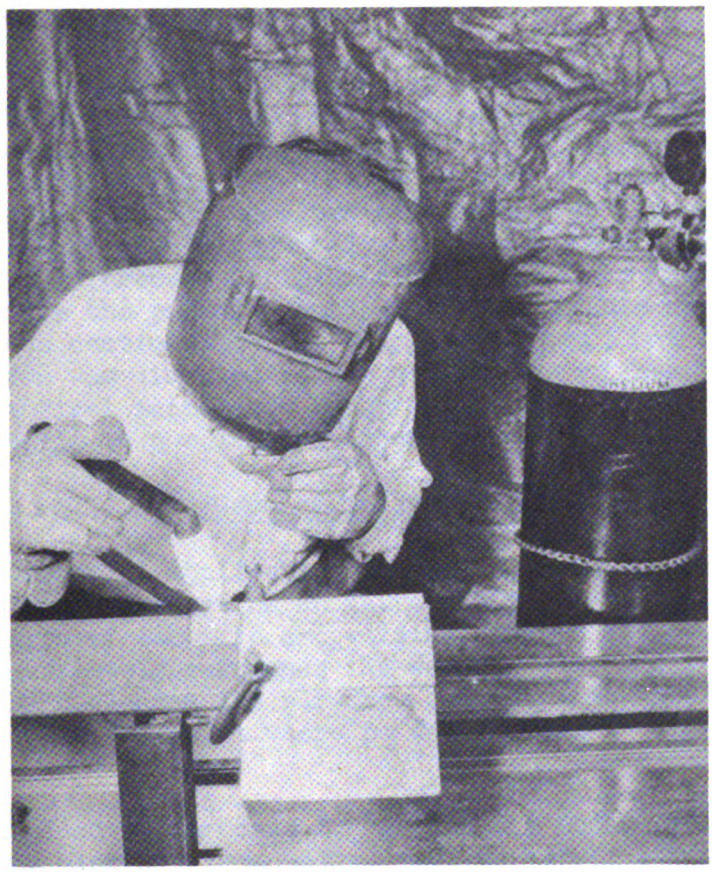

Figure 27. - Manual welding, using helium-shielded arc process.

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installation of similar purifiers on all units at the Bureau's Exell Helium Plant, and for the other plants when needed, and several of the purifiers were built. A number of these were installed at the Exell plant, and all helium subsequently shipped was of a purity of 99.8 percent or better. The impurity is chiefly hydrogen, and consideration is being given to means for removing it if and when it may seem desirable. Experiments with the charcoal purifiers were limited to those possible in routine operation of units now installed; too few units were available to permit extensive experiments without possible interference with plant operation. When additional units are installed it is planned to renew experimental work in an effort to improve operation and obtain still higher purity with the same or with modified equipment. Two views of one of the units are shown in figure 26.

Other process-development research being conducted is a method for separating helium from natural gases at pressures up to about 3,000 psi. Natural gases of unusually high helium content have been found where the pressure of the gas coming from the well is of that order of magnitude. Previously used processes were designed for natural gas at a pressure not exceeding about 600 psi. Last year's report described the beginning of work leading to development of a process for extracting the helium from this gas without first having to reduce the pressure and lose the available energy contained in it. This work was continued during the present year, but on a reduced scale. Investigation was directed to the development of heat exchangers for the process and practical methods of construction were worked out so that the exchangers can be built in a relatively short time.

Uses of Helium

The postwar commercial application of helium receiving the greatest impetus from industry is its use as an inert gas in the shielded-arc welding process. In this type of electric arc welding, the inert helium is discharged from a nozzle and completely surrounds the welding electrode, eliminating harmful oxidation by excluding the air from contact with the hot metal until the metal has cooled to the point where no damage will be done to it by contact with the air.

The helium shielded-arc process for welding is being widely employed in industry for welding aluminum, magnesium, copper, copper alloys, stainless steel, and high-alloy carbon steel. Specific uses of the helium-arc process now include the welding of aluminum barrels, the welding of copper-alloy tanks, the welding of stainless steel and inconel tubing, the welding of magnesium aircraft parts, the welding of silicon transformer steels, and the welding of alloys and metals made available recently, such as Fernico and titanium.

The rapid expansion of our Nation's aircraft program, as well as the expansion of the light-metals industry, has brought about wide acceptance of helium inert-arc welding. Other forms of welding are not as satisfactory, or else they are not acceptable at all for welding aluminum and magnesium; consequently, the importance of helium to industry, as well as to our military program, can scarcely be overemphasized. Manual welding, using the helium shielded-arc process, is shown in figure 27.

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Helium in Metallurgy

Helium is now being used for numerous metallurgical processes other than welding.

One of the outstanding developments of the Bureau of Mines has been development of a process for making metallic titanium. The process utilizes an atmosphere of helium to prevent gas pick-up. The helium atmosphere is necessary, since titanium readily combines with oxygen, nitrogen, and hydrogen. Metallic titanium has great possibilities because it is light and has high strength and good corrosion resistance.

Helium is used in powder metallurgical processes for making cigarette-lighter flints. The metal used for flints is highly inflammable and is processed using a helium atmosphere.

Other metallurgical uses for helium include the flushing of molten stainless steel to remove hydrogen and impurities and the annealing and heat treatment of metals in an atmosphere of helium to prevent oxidation and contamination.

One phase of the metallurgical work involves an investigation of the effects of different impurities found in helium on welds made by the helium inert-arc process. Before March 1948 helium produced at the Bureau of Mines plant had a purity of 98.2 percent. This helium proved satisfactory for welding magnesium and stainless steel but not too satisfactory for welding aluminum. Studies in the Bureau of Mines laboratories showed that even minute percentages of nitrogen, water vapor, or oil vapor in helium had a pronounced and often adverse effect on aluminum welds. It was found that, by keeping the impurities to a minimum and producing helium of a purity of 99.8 percent or better, satisfactory welds could be made on aluminum. As a result of these studies by the Bureau of Mines, new equipment was installed so that the helium plant now is producing all of its helium at a purity of 99.8 percent or better.

The metallurgical investigations of welds necessitate much more than visual examination. For such investigations, numerous microscopic examinations, tensile tests, bend tests, hardness tests, and X-ray examinations are required. New equipment obtained recently by the Bureau for this purpose include a 200,000-kilovolt Westinghouse X-ray machine, a 20,000-pound Tate Emery tensile testing machine, and a Brinell hardness tester. The X-ray machine is shown in figure 28.

Medical Use of Helium

Medical uses of helium consumed almost 10 percent of the total helium sold for non-Federal commercial uses. When employed for medical treatment, it is used to dilute oxygen and form an artificial breathing atmosphere that is administered in treatment of severe asthma cases and other disorders of the lungs, chest, and throat. It also is used mixed with oxygen in administering anesthesia preparatory to surgical work. The helium itself does not

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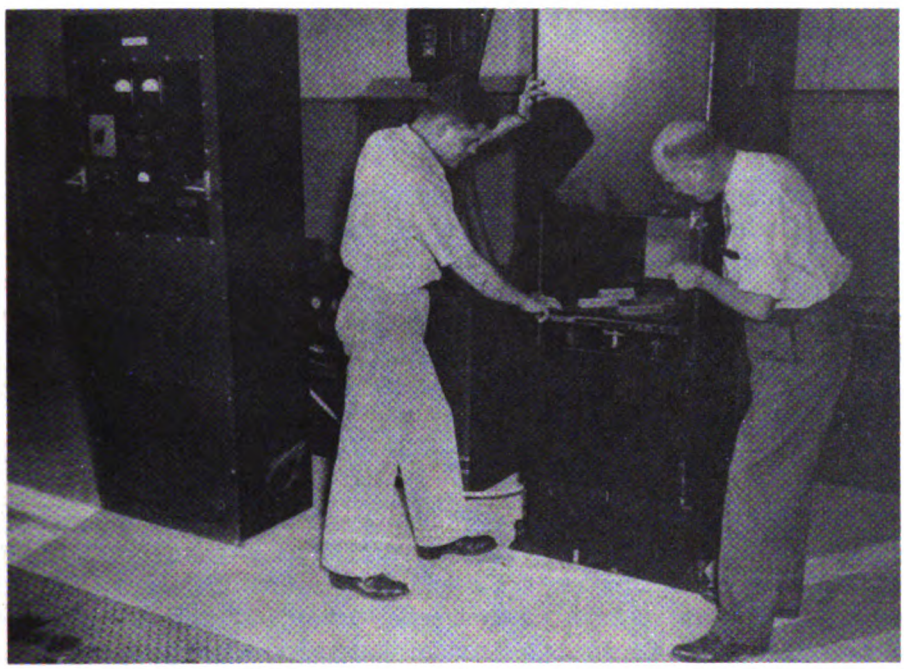

Figure 28. - X-ray equipment used in photographing welds made by helium-shielded arc process.

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have any known curative properties but owes its medical value to some of its peculiar physical properties. It is extremely light compared to ordinary air; consequently, much less muscular effort is required to breathe the mixture of oxygen and helium than to breathe ordinary air. Thus, in extreme cases of asthma and other chest and throat disorders, the patient can breathe the light helium-oxygen mixture with ease when otherwise he might not have enough muscular strength to continue breathing ordinary air. Thus, the artifical air enables him to survive the crisis until a normal recovery cycle sets in and he is able to continue on ordinary air. When used in connection with the administration of anesthesia, helium serves a useful purpose in reducing or eliminating the possibility of explosion. The vapors of most anesthetics are explosive when mixed with air, and sometimes these vapors are ignited during the course of surgical work. As the patient's lungs are filled with the explosive mixture, the results are often fatal. When the artifical helium-oxygen mixture is administered during anesthesia, however, the presence of the helium reduces and may eliminate the conditions under which an explosion may occur.

Helium as a Tracer Gas

The Bureau's work on developing helium as a tracer gas continued throughout the year. For such use, helium is mixed for short periods in small concentrations with natural gas that is being pumped back into oil- and gas-producing formations. The appearance of this tracer helium in gas that is produced from wells in various parts of a field reveals valuable information on the direction and rate of travel of the injected gas. Helium can be detected readily even though it is present in only very small concentrations; this ease of detection, along with its chemical inactivity and low solubility, makes helium ideal for use as a tracer gas.

Bureau of Mines engineers assisted the operators of the West Edmond, Okla., oil field in planning a helium tracer-gas project in that field, supervised the initial phase of injecting the helium, and trained the operators' personnel to carry on the project. The helium tracer-gas project was part of a large-scale test program conducted by the operators to obtain data needed in designing and constructing a multimillion-dollar gas-injection plant and was instituted to determine whether the injected gas would channel or bypass through the formation. The operators conducted later phases of the project with only occasional assistance from the Bureau of Mines.

A helium tracer-gas project begun last year by the operators in the Shuler, Ark., field was continued through the present year, with occasional additional assistance from the Bureau engineers. It is not yet complete. Bureau of Mines engineers collaborated with the operators in interpreting the data that were collected and in making broad plans for continuing the work. A report of the project is to be prepared and published by the Bureau when the work is complete.

Projects that were started by the Bureau in fiscal year 1946 in the Cabin Creek, W. Va., and Slaughter, Tex., fields were virtually completed during the present year, and progress was made on the preparation of manuscripts

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reporting the findings. It is anticipated that these reports will be published during the coming year. The transfer of helium from a tank car to a tank truck for moving to the West Edmond field, Okla., tracer project is indicated in figure 29.

HELIUM PRODUCTION

The production of helium by the Bureau of Mines this year totaled 67,486,500 cubic feet, an increase of approximately 6.8 percent over last year. Forty-three percent of the helium produced was allocated to various Government uses, 28 percent to commercial users, and the remaining 29 percent was injected into the Government-owned Cliffside natural-gas field. The entire amount was produced at the Exell Helium Plant, near Amarillo, Tex., while the Bureau's three additional helium-production plants remained in standby status. The Exell plant is situated on a pipe line that transports helium-bearing natural gas from the Texas Panhandle gas field to commercial markets whether or not the helium is extracted, and if the helium is not extracted before the gas is used as a fuel it is lost forever. Two of the standby plants, if operated, would take gas from Government-owned fields; and, if the plants are not operated, the helium stays in the formation until needed. Thus, the present program of operation is one involving conservation of the Nation's resources. The Exell plant, by operating at normal capacity, again was able to produce more than the current demands for helium, and the surplus helium thus produced was transported by available Government-owned pipe lines to the Cliffside natural-gas field and injected into the formation for storage awaiting future needs. The cost of operating the plant at normal capacity was only slightly more than if it had been operated at reduced capacity. Thus the additional helium was recovered at a very small cost. The return of surplus helium to the Government-owned Cliffside natural-gas field was begun in 1945, and since that time a total volume of slightly more than 77 million cubic feet of helium has been conserved in this manner for future use.

The yearly and cumulative volumes of helium that have been produced by the Bureau of Mines since the start of helium production in 1926 is shown in figure 30.

The Exell Helium Plant was operated 355 days during the year with an average production exceeding slightly the maximum capacity for which it was designed. During the last 4 months of the year all of the helium production was required to satisfy the demand, and none was sent to storage in the Cliffside field. The Bureau has three production plants in addition to the Exell plant, but all three are in standby status as a result of decreased demands for helium following the close of the recent war. Those are the Amarillo Helium Plant, near Amarillo, Tex., the Otis Helium Plant, near Otis, Kans.; and the Navajo Helium Plant near Shiprock, N. M. The Amarillo plant and the Navajo plant each take helium-bearing natural gas from fields owned by the Government; but the Otis plant, like the Exell plant, obtains its supply of helium-bearing natural gas from commerical pipe lines that are taking the gases to fuel markets. Thus, the Bureau could make available to industry many additional millions of cubic feet of helium that otherwise are going to waste and, at the same time, maintain the present relatively large reserves of helium in the gas fields owned by the Government.

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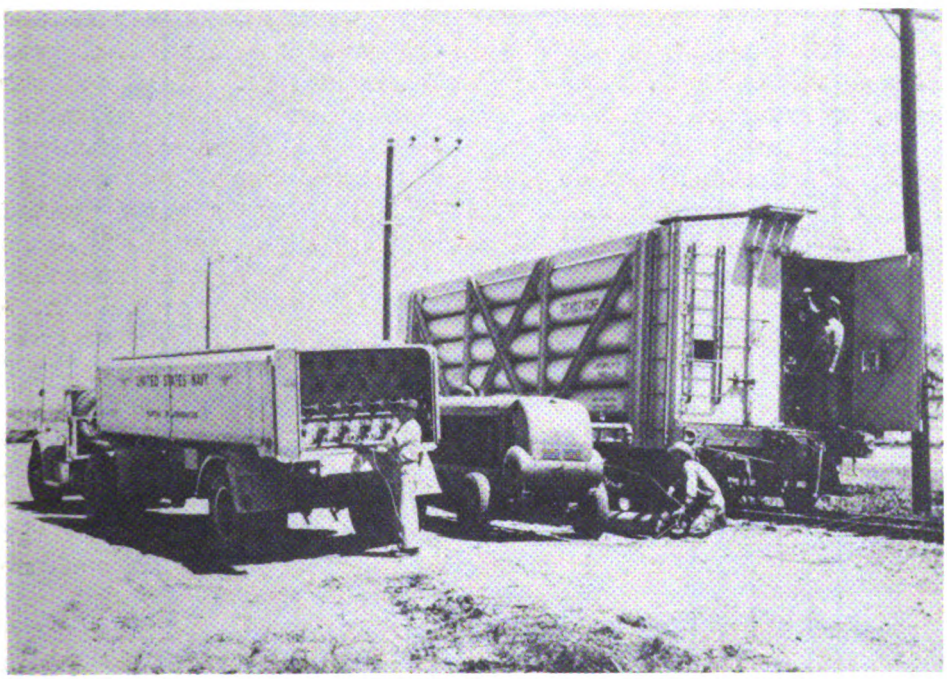

Figure 29. - Transfer of helium from railway tank car to motor-transport trailer, utilizing portable helium compressor, West Edmond field, Okla., helium tracer project.

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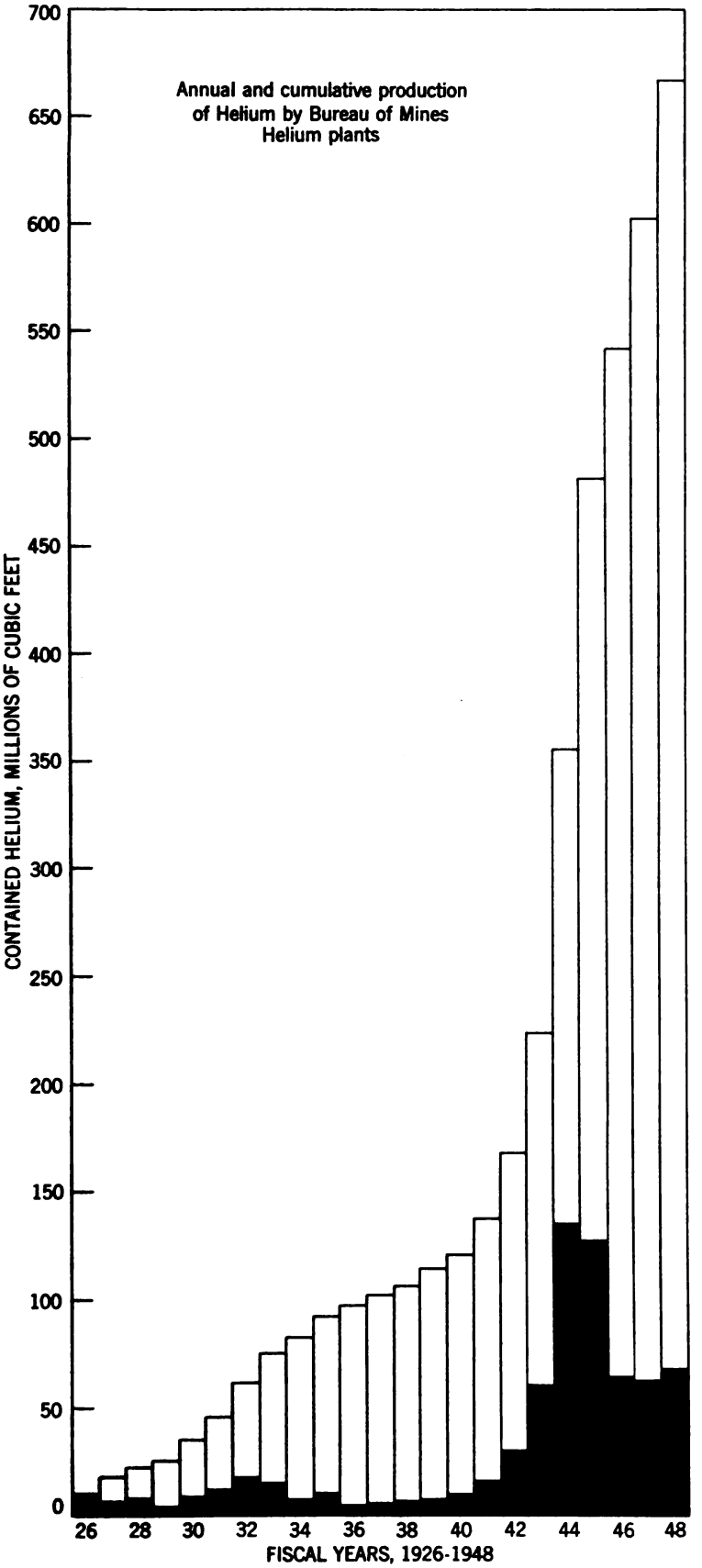

Figure 30. - Yearly and cumulative volumes of helium produced by Bureau of Mines.

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